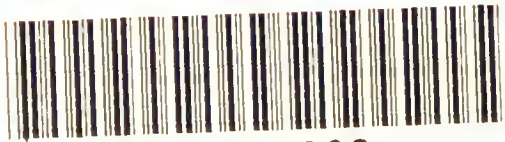
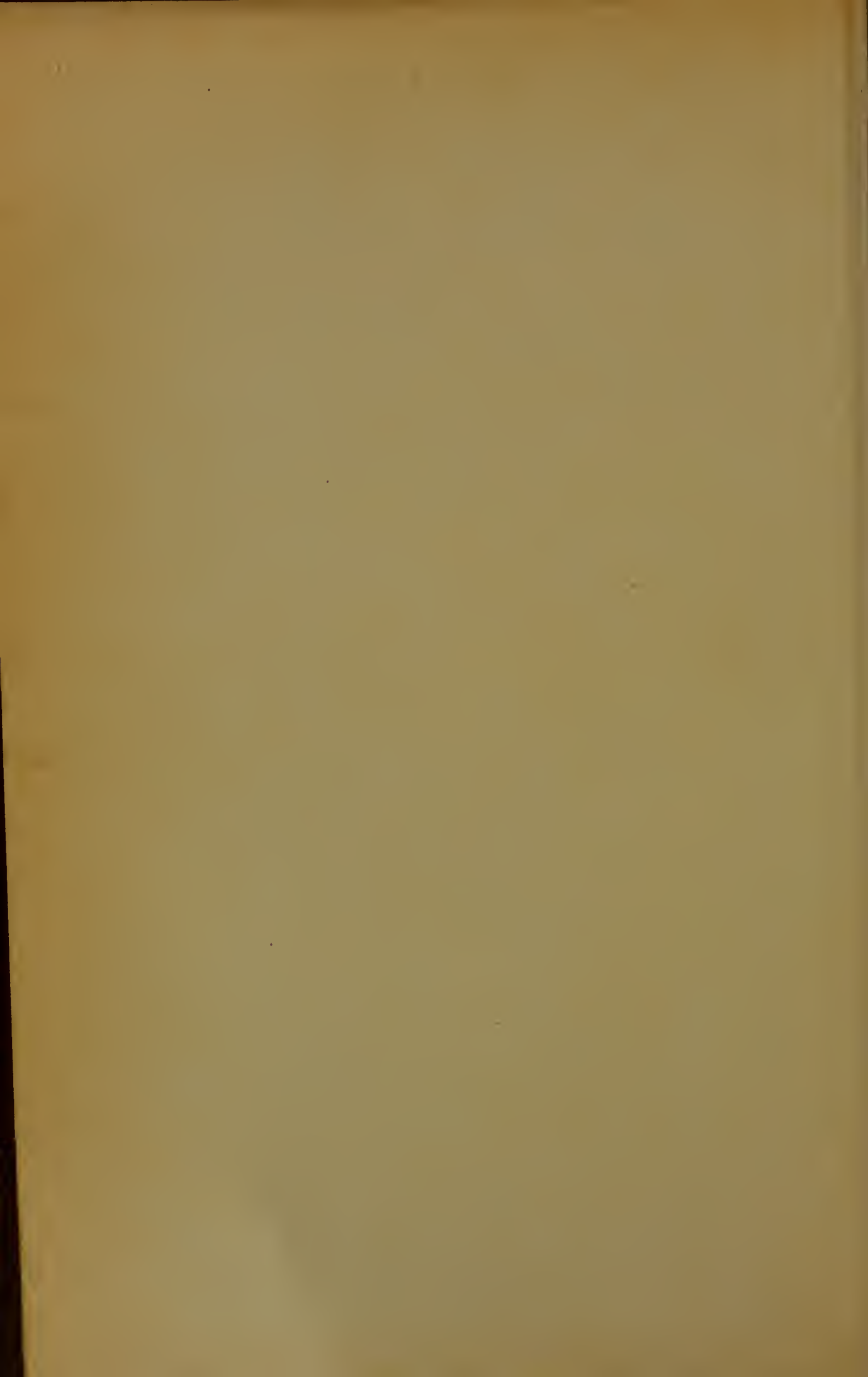


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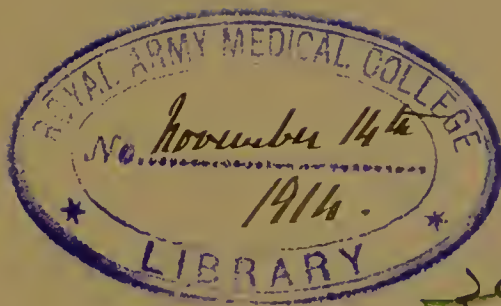
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TECHNICAL METHODS OF
CHEMICAL ANALYSIS

TECHNICAL METHODS OF CHEMICAL ANALYSIS

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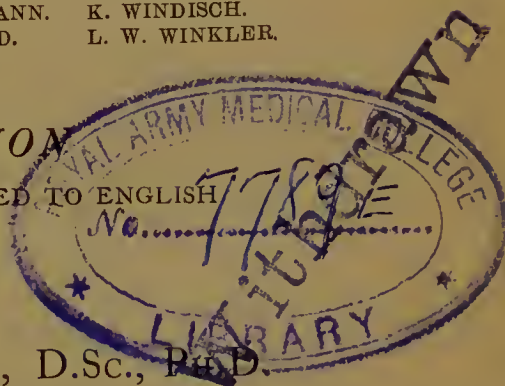
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SUGAR

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Prefatory Note.—In preparing this section, Dr von Lippman's text has been given in full, and some further matter has been added to bring it up to date. Some years ago much of the matter might justly have been regarded as extraneous so far as the English reader is concerned. Now that a sugar factory is in existence in this country, and has been working through two campaigns, it is hoped that a British sugar industry will before long be established; it has, therefore, been considered desirable not to omit anything, especially as Prof. von Lippmann's selected methods are undoubtedly the most trustworthy. The additions which have been made refer especially to methods devised here. The section dealing with cane sugar products may appear to be unduly subordinate to that on beet sugar, in view of the large amount of cane sugar imported into this country, but for the reasons given in the text under "Products of the Cane Sugar Industry," it has been regarded as desirable to commence the description of the technical methods of analysis employed in the sugar industry with the more reliable, and at the same time generally applicable methods that have been worked out in connection with the examination of beet sugar.

I. THE SUGAR-BEET.

The accuracy and practical value of an analytical investigation depend to a great extent on the careful selection of an average sample,¹ especially as the beetroot itself is far from homogeneous. Not only are the variations of the sugar-content in different roots grown in the same field often very great, but even in the individual root the sugar is by no means uniformly distributed.

It is a well-known fact that the percentage of sugar varies in

¹ Cf. H. Claassen, *Z. Ver. deut. Zuckerind.*, 1896, 46, 98; also P. Herrmann, *Verlustbestimmung und Betriebskontrolle der Zuckerfabriken*, 1905.

different zones of the root, and this is illustrated by the following experiment recently made by Ling.¹ Some roots of an average weight of 1'lb. 10 ozs. were analysed, with the following results:—

Sugar in roots	15.3 per cent.
Specific gravity of the juice (Brix)	18°8
Sugar in the juice	17.2 per cent.
Coefficient of purity	91.5 „

One of the roots was cut into transverse sections, as shown in Fig. 64, and the sugar-content of each section estimated.

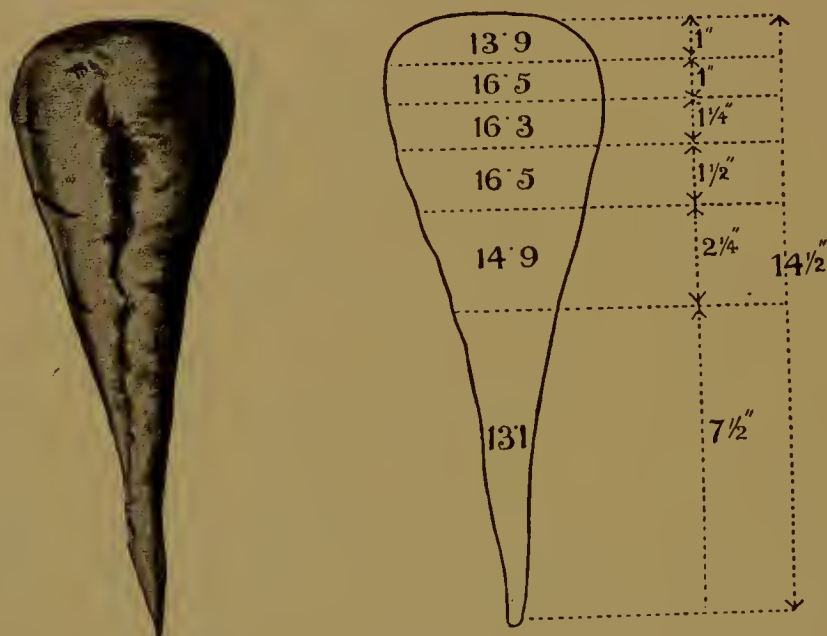


FIG. 64.

Where average samples of whole roots are required, it is best to use the sample taken during the unloading of the weigh-bridge or carts for the purpose of estimating the amount of adhering soil. Since this sample amounts to at least several hundredweight, a further selection is necessary. This selection is always carried out according to certain arbitrary rules, since an absolutely representative sample can naturally never be obtained. The selected roots are washed or brushed with a hard brush, and as a rule are freed from the stalks and thinner offshoots unsuitable for sugar manufacture. Frozen roots are left to thaw slowly in a moderately warm room prior to analysis.

The best method for sampling a given quantity of roots, *e.g.* consignments from abroad, is that specially prescribed by the Austrian chemists.² If only a few roots are sent, the whole roots are to be

¹ *Annual Report of British Sugar-Beet Council*, 1911, p. 17.

² *Jahr- und Adressenbuch der Zuckerfabriken und Raffinerien Österreich-Ungarns*, 1909-10, 81.
See also Ledoux, *Sucrierie Belge*, 1909, 38, 218.

ground (see below) in order to obtain a good average sample; in the case of a large number, an aliquot part of each root, corresponding to its size (a longitudinal section), is used for grinding. In the case of a sample for sugar estimation, not more than twenty roots should be used; if the sample sent for analysis contain more than this number, it should be divided into several smaller samples of equal weight, the arithmetical mean of all the results being taken as the percentage of sugar in the whole sample.

In order to obtain uniform samples, *e.g.* for the purpose of sending to two chemists for analysis, the trimmed and cleaned roots should be weighed and placed in a series according to weight or size, beginning with the smallest and ending with the largest. The roots 1, 3, 5, 7, 9, etc., constitute one sample, and the roots 2, 4, 6, 8, 10, etc., constitute the other.

In order to allow for drying and consequent change in the composition of the beetroot, the total weight of the cleaned roots should be determined when the sample is sent, and made known to the analyst.

A good average sample may be obtained much more readily from the fresh beet slices than from the whole root.¹ The slices are removed as quickly as possible from the slicing machine, and samples of equal weight are collected in a bottle provided with a well-fitting stopper. The contents of this bottle must be thoroughly mixed every three or four hours, or in the case of decayed roots, every hour; automatic sampling machines have not proved satisfactory. In cases where the scalding process is employed, care must be taken that the slices do not absorb steam.

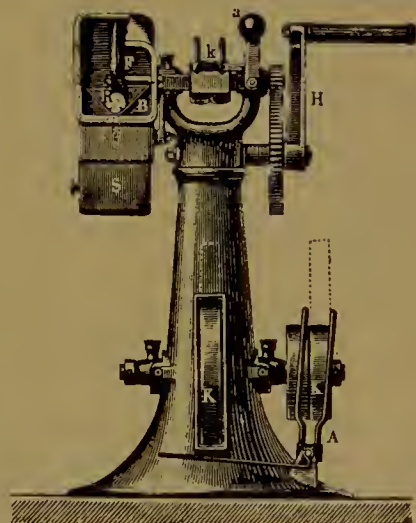


FIG. 65.

For the purpose of analysis, both roots and slices must be subjected, in sufficient quantity,² to a thorough disintegration, in which operation loss of juice must be avoided. In the case of whole beetroots, an extremely fine impalpable pulp may be obtained by means of Kiehle's beetroot grinding machine (Fig. 65), or Keil and Dolle's³ boring machine, or the Stanek-Perner mill which is much used in Austria.

In the case of a very large number of analyses carried out by the

¹ For the correct method of sampling, see *Anweisungen für einheitliche Betriebsuntersuchungen in Rohrzuckerfabriken*, Berlin, 1910, p. 2.

² According to Le Docte, the preparation and use of insufficient samples may cause serious errors (0.4 per cent. or more)—*Sucrerie Belge*, 1910, 39, 128.

³ *Z. Ver. deut. Zuckerind.*, 1889, 39, 584.

hot aqueous digestion method, Kiehle's grinding machine was employed with most satisfactory results (A. R. Ling).

Beetroot slices may be reduced to a similar finely divided pulp by means of the crushing machine also constructed by Kiehle.¹ A satisfactory pulp may also be obtained both from beetroot and beetroot slices by means of the special contrivances of Herles² and of Pellet.³ From whole beetroots a coarser but uniformly ground pulp, which is quite suitable for most purposes, may be obtained by means of hand graters, whilst meat-mincing machines, which have been much improved recently, may be employed for slices. Finally, the boring machines constructed by Dehne of Halberstadt⁴ and by M. Wahrendorf of Oschersleben, should be mentioned. These machines, even when worked by hand, give a very uniform pulp without any loss of juice. All these machines must be kept clean and in good working order.

Prior to analysis, the pulp (preferably about 1 kg.) is carefully mixed and placed in a covered vessel. Owing to its tendency to ferment, and the readiness with which it loses water, the quantities of pulp required for each determination must be weighed out successively as quickly as possible, and the vessel must be covered again directly a portion has been removed. According to Pellet,⁵ however, the pulp may be kept unchanged for three to five hours, without addition of any preservative, in well-stoppered vessels at the ordinary temperature.

A.—ESTIMATION OF SUCROSE.

In accordance with the method published by the "International Commission for Standard Methods of Sugar Analysis" in 1900,⁶ the amount of substance to be weighed out for the determination of sucrose is 26 g. This quantity is the "normal weight" for the Soleil-Ventzke-Scheibler polarimeter, the scale of which is generally used (excepting in France), and its employment is taken for granted in the various modified, half-shadow polarimeters designed by Schmidt and Haensch⁷; hence, the above-mentioned International method of 1900 will, in future,

¹ *Z. Ver. deut. Zuckerind.*, 1892, 42, 281; this machine causes a slight loss of juice and heating of the pulp.

² *Z. Zuckerind. Böhm.*, 1900, 25, 209; 1901, 26, 167.

³ *Sucrerie indigène*, 1903, 62, 644; this instrument is designated "Sans Pareil."

⁴ *Zentralbl. für die Zuckerindustrie der Welt*, 1897, p. 65.

⁵ *Bull. Assoc. Chim. Sucr.*, 1905, 23, 539.

⁶ *Z. Ver. deut. Zuckerind.*, 1900, 50, 357; *J. Soc. Chem. Ind.*, 1900, 19, 1151.

⁷ Precise directions for use are always supplied with the instrument. Concerning the control of the instrument with normal quartz plates, and the serious errors which are caused by the compression of these plates (and consequently by variations in temperature), cf. Herzfeld, *Z. Ver. deut. Zuckerind.*, 1899, 49, 1, and F. Wiechmann, *ibid.*, p. 266, and 1900, p. 902; *J. Soc. Chem. Ind.*, 1900, 19, 1027. Concerning the errors due to the construction and manipulation of the polarimeter, their detection and elimination, cf. Kovar, *Oesterr.-Ungar. Zeitschr.*, 1901, p. 448.

be carried out exclusively with the use of half-shadow instruments. According to the definition of the "Physikalisch-Technische Reichsanstalt," the 100-point of the saccharimeter is fixed as follows¹:—A solution containing 26 g. of chemically pure sucrose weighed in air (density, 0.0012) with brass weights (density, 8.4), per 100 c.c. at 20° (or 26.016 g. of sucrose if the weight is reduced to a vacuum), is polarised at 20°² in a 200 mm. tube. The metric cubic centimetre is here referred to, namely, the volume occupied by 1 g. of water at 4°, weighed *in vacuo*, corresponding to the volume occupied by 0.997174 g. of water at 20°, weighed in air and with brass weights. Each scale division evidently corresponds to 0.26 g. of sucrose in 100 c.c. of solution; hence, if 26 g. of a substance containing sucrose be weighed out as described, dissolved in water and made up to 100 c.c., and the rotation determined in a 200 mm. tube at 20°, the percentage of sucrose in the substance is obtained directly. To obtain correct readings with the use of white light, it must be remembered, as O. Schönrock has observed,³ that different sources of white light, especially with different observers, always cause appreciable discrepancies which are only eliminated if the light is transmitted through a 6 per cent. solution of potassium bichromate of 1.5 cm. thickness.

In actual practice, the "old" normal weight of 26.048 g., which refers not to metric cubic centimetres but to Mohr's cubic centimetres,⁴ is still in use in many places, *e.g.* in sugar factories:—26.048 g. of sucrose (weighed in air) dissolved in 100 Mohr's cubic centimetres at 17°·5, and examined in a 200 mm. tube at 17°·5 rotate the plane of polarisation through 100° (Ventzke), and each scale division corresponds to 0.26048 g. of sucrose in 100 c.c. of solution.

It should be stated here that according to Herzfeld's investigations correct polarimetric readings can only be obtained if the temperature of the polarimeter, of all the apparatus, and of the laboratory is maintained constant for at least three hours before observations are taken. If the temperature at the time of reading differs by more than a few degrees from the standard (20° or 17°·5), the mere adjustment of the zero point is not a sufficient control of the apparatus, since the value of the scale alters with the temperature. In this case the value of the controlling quartz plates (which must not be cemented in) must be determined by means of a normal solution of chemically pure sucrose for a definite temperature (generally the prevailing one), which temperature must be maintained in all the remaining analyses. Otherwise, serious errors, which may amount to as much as ± 0.65 , are unavoidable.

¹ *Z. Ver. deut. Zuckerind.*, 1901, 51, 542.

² *Ibid.*, 1900, 50, 997.

³ *Ibid.*, 1904, 54, 521; *J. Soc. Chem. Ind.*, 1904, 23, 561.

⁴ A cubic centimetre (Mohr) is the volume occupied by 1 g. of water weighed in air with brass weights at 17°·5—Mohr, *Chemisch-analytische Titrimethode*, 1886, pp. 44-50.

The following Table, giving the temperature variations in the Ventzke reading per 1° according to different observers, is quoted from C. A. Browne's *Handbook of Sugar Analysis*.

Andrews (<i>Technology Quarterly</i> , Mass. Inst. Technology, May (1889), p. 367)	0.0300
The United States Coast and Geodetic Survey	0.0293
Wiley (<i>J. Amer. Chem. Soc.</i> , 1899, 21, 568)	0.0314
Prisen Geerligs (<i>Archief Java Suikerind</i> , July 1903)	0.0300
Watts and Tempny (<i>West Indian Bull.</i> , vol. iii., p. 140)	0.0310
Average	0.0303

The method of estimating the percentage of sucrose in beetroots, which consists in polarising the juice and multiplying the percentage of sugar in the juice by the factor 0.95, is arbitrary and untrustworthy, and is to be replaced by an estimation of the sugar in the beetroot itself. For this purpose one of the following methods may be used:—(1) Hot alcoholic extraction, (2) Hot alcoholic digestion, (3) Hot aqueous digestion, (4) Cold aqueous digestion. Owing to its tediousness, and numerous sources of error, Stammer's method of cold alcoholic digestion¹ is no longer used.

Alcoholic Extraction.

When the highest accuracy is required, the method of alcoholic extraction originally proposed by Scheibler² and improved by Sickel³ is now preferred, since when properly executed it not only yields accurate results, but also possesses an important advantage in that it is possible to determine at any time whether the whole of the optically active material has been extracted, a control which does not appear to be equally practicable with the various "digestion methods."

The apparatus commonly used for the purpose of alcoholic extraction is the well-known Soxhlet's syphon extractor modified by Sickel, which is shown in Fig. 66. Herzfeld's modification,⁴ shown in Fig. 67, is very suitable and very readily manipulated. At the bottom is the extraction vessel, A, consisting of two parts each of about 100 c.c. capacity; these are connected by a short tube of about 1 cm. diameter; a mark is etched upon this tube up to which the lower half contains exactly 100 c.c. (at $t = \frac{20^{\circ}}{4}$). Above the extracting vessel, A, is Muller's⁵ extraction apparatus, B, which permits of the removal of

¹ *Z. Ver. deut. Zuckerind.*, 1883, 33, 206; 1884, 34, 73.

² *Neue Zeitschrift für Rubenzuck. Ind.*, iii., p. 242.

³ *Z. Ver. deut. Zuckerind.*, 1879, 29, 692.

⁴ *Z. Ver. deut. Zuckerind.*, 1901, 51, 334; cf. also Baumann, *ibid.*, 1890, 40, 689.

⁵ *Z. angew. Chem.*, 1892, 5, 232.

samples of the extracting liquid by means of a tube at the side which is generally closed with a stopper; below the inner opening of the syphon tube a circular piece of wire gauze of 3 cm. diameter is placed. At the top is the Soxhlet's glass condenser. The whole apparatus is placed in a water-bath of such depth that the liquid boils in A sufficiently quickly to cause the syphon to come into action in three or four minutes.

For the estimation, 26 g. of beetroot pulp are weighed out in a



FIG. 66.



FIG. 67.

shallow-lipped nickel dish. Ground beetroot pulp is best mixed with clean glass beads to insure as uniform a distribution of the pulp as possible, and to prevent the formation of lumps. The weighed portion is at once¹ thoroughly mixed, by means of a glass rod with 3 c.c. of a solution of basic lead acetate and a few cubic centimetres of 90 per cent.

¹ Wiskirchen, *Z. Ver. deut. Zuckerind.*, 1894, 44, 698.

alcohol. The basic lead acetate used in all analyses is prepared as follows:—3 parts of lead acetate, 1 part of litharge, and 10 parts of water are used. The lead acetate and the litharge are thoroughly mixed, and after addition of one-twentieth of the above-mentioned quantity of water, the mixture is stirred on the water-bath until the original yellow colour is changed to reddish-white. The remainder of the water is then added, the solution being poured into a stoppered flask to clear, and finally filtered. The clear, colourless solution thus obtained has a sp. gr. of 1.235-1.240. This early addition of basic lead acetate solution not only causes the conversion of non-sugar substances into insoluble lead compounds, but accelerates the absorption of water by the beetroot fibre, and thereby reduces the time necessary for extraction. This mixture is washed into the extraction apparatus B with 90 per cent. alcohol, care being taken to avoid any loss of substance; the pulp is loosely and uniformly distributed in the lower part of the extraction apparatus, and the glass rod is rinsed with alcohol. The amount of alcohol used must be such that the vessel A finally contains about 75 c.c. of liquid. The extraction process is now begun. After two hours a sample of the extracting liquid is withdrawn and tested by means of the α -naphthol reaction proposed by Ihl¹ and improved by Muller and Ohlmer.² This test is best carried out as follows, according to the recommendations³ of the Austro-Hungarian Official Sugar Analysts:—A few drops of the solution to be examined are diluted to 2 c.c. with distilled water in a test tube, mixed thoroughly with 2 drops of a freshly prepared 20 per cent. alcoholic α -naphthol solution, and finally 10 c.c. of pure concentrated sulphuric acid, free from nitric acid, are carefully poured down the side of the test tube in order to avoid mixing. If, without further agitation, a violet-coloured ring is formed at the junction of the liquids, sugar is still present in the pulp and the extraction must be continued. As soon as sugar is no longer to be detected, the vessel A is cooled to 20°, its contents being made up to the mark (whereby the interior surface of the upper spherical part of the vessel is well rinsed) and filtered. The filtrate is polarised in a 200 mm. tube, the reading corresponding to the percentage of sucrose in the beetroot. With the polarisation of this, as of all alcoholic solutions, special attention must be paid to the exact adjustment to the normal temperature, and to the use of perfectly clear homogeneous filtrates free from any tendency to become cloudy; it is best to reject the first portion of the filtrate, since the filter paper may at first absorb sugar.⁴

When the process is carried out as above described, the complete extraction of the sugar generally takes a long time, and in this respect

¹ *Chem. Zeit.*, 1885, 9, 231.

² *Deutsche Zuckerindustrie*, 1892, p. 419.

³ *Oesterr.-Ungar. Zeitschr.*, 1897, p. 509; 1901, p. 664.

⁴ *Cf. Zentralbl. für die Zuckerindustrie*, 1905, 14, 193.

great improvements have been made by A. Herzfeld¹ and by A. Le Docte.²

According to Herzfeld, a 100 c.c. flask is filled to about half its capacity with 26 g. of pulp, together with alcohol of not more than 90 per cent. concentration and 3-5 c.c. of basic lead acetate solution. The flask, fitted with a reflux tube, is placed in a water-bath for ten to fifteen minutes, its contents then being introduced into the extraction apparatus shown in Fig. 67. As a result of this preliminary treatment the extraction is rapid from the beginning, and the time required for complete extraction is shortened by several hours. If the pulp is very finely divided, the extraction apparatus is connected to an aspirator, whereby the alcohol is rapidly brought to a state of vigorous ebullition, and the analysis is completed in two to three hours.

Le Docte shortens the process by using an improved condensing and distributing device for the alcohol, together with an aspirator. 26 g. of pulp are heated with 120-150 c.c. of 75 per cent. alcohol, and after the alcohol in the extraction apparatus has been syphoned over once, heating is continued for twenty-five to thirty minutes; during this period the syphon acts twelve to fifteen times, and this suffices for complete extraction. Samples of the solvent may be withdrawn at any time by means of a glass tube introduced through the condenser.

Digestion Methods.

In the case of the various digestion methods, the extraction of the sugar is effected directly in a sufficiently wide-necked graduated flask, and the polarisation of the filtrate, corrected for the volume occupied by the beetroot fibre, gives the percentage of sucrose in the beetroot directly. According to Rapp, the fibre from 26 g. of beetroot pulp occupies a volume of 0.6 c.c. The solution is either made up to 100 c.c. and the polarisation reading multiplied by 0.994 or graduated flasks of 100.6 c.c. or 201.2 c.c. capacity are employed (see below). Of course, care must be taken that the air enclosed in the pulp is completely removed, and the prescribed methods of working,³ which have been based on long experience, must be followed exactly, since otherwise many sources of error are introduced, and these have from time to time brought the various methods of digestion into disrepute.⁴

(a) The Warm Alcoholic Digestion Method of Rapp-Degener⁵

¹ *Z. Ver. deut. Zuckerind.*, 1909, 59, 627.

² *Sucrerie Belge*, 1909, 38, 2.

³ Cf. amongst others, Krüker, *Z. Ver. deut. Zuckerind.*, 1894, 44, 322; Baumann, *Korrespondenzblatt*, 1894, No. 17.

⁴ Concerning alcoholic digestion, see, e.g., Weistberg, *Bull. Assoc. Chim. Sucr.*, 1899, 17, 237.

⁵ *Z. Ver. deut. Zuckerind.*, 1882, 32, 786.

is difficult and liable to error; according to the report of the Austro-Hungarian Official Analysts,¹ it is only to be used when specified, and is best carried out as follows:—

Twice the normal weight (52 g.) of beetroot pulp is weighed in a nickel dish and rinsed with alcohol of 90-92 per cent. concentration (by volume) into a 201.2 c.c. graduated flask (see p. 547), the neck of which is widened and funnel-shaped. Four c.c. of basic lead acetate solution are then added, the flask shaken several times, and enough 90-92 per cent. alcohol added to fill the flask to about four-fifths of its volume. A condensing tube, about 50 cm. long and 10 mm. internal diameter, the lower end of which is cut obliquely, is then fitted to the neck of the flask, and the apparatus is placed in an oblique position in a water-bath previously heated to boiling. When the liquid in the flask has begun to boil, it is kept gently boiling for twenty minutes; the flask is then removed from the water-bath, the cork and condensing tube are rinsed into the flask with alcohol, and the latter filled, without cooling, nearly to the mark with alcohol. Then the flask is placed in the hot water-bath again until bubbles begin to rise through the alcohol, cooled to 20°, and filled exactly to the mark with alcohol. After having been vigorously shaken the solution is filtered and its rotation determined in a 200 mm. tube. (In a few laboratories it is considered indispensable to allow the stoppered flask to stand for thirty minutes with repeated shaking.) The percentage of sucrose is thus obtained directly. If a 201.2 c.c. flask is not available, a 200 c.c. flask may be used; in this case, however, only 51.8 g. of pulp must be weighed out instead of 52 g.² If the pulp is not very fine and homogeneous, and if the amount of basic lead acetate solution added is not so regulated that any precipitation of sucrose is avoided, the results obtained by this method may be too low by 1 per cent. or even more.

(b) The Warm Aqueous Digestion Method suggested by Pellet is carried out as follows, according to the above-mentioned Austro-Hungarian report, in the modified form due to Herles³:—

Half the normal weight of pulp, which may be of coarser quality, is weighed out for each 100 c.c. of the flask capacity (52 g. in 400 c.c. is most suitable), and washed into the flask with hot water, the temperature of which must not fall below 90°; after addition of basic lead acetate solution (4.5 c.c. for each 26 g. of pulp), the flask is filled nearly to the mark with hot water, thoroughly shaken and allowed to stand. After half an hour's digestion, the flask is cooled, filled to the mark, the solution filtered and its rotation determined in a

¹ *Oesterr.-Ungar. Zeitschr.*, 1897, p. 509; 1901, p. 664.

² *Deutsche Zuckerindustrie*, 1889, p. 531.

³ *Oesterr.-Ungar. Zeitschr.*, 1897, p. 510; 1901, p. 664.

200 mm. tube. The reading when doubled and multiplied by 0.994 gives the percentage of sucrose. This multiplication is of course unnecessary if the flasks employed are graduated so as to allow for the space occupied by the beetroot fibre.

Herzfeld recommends the following method¹:—26 g. of pulp are triturated in a metal dish with 5-6 c.c. of basic lead acetate solution; the mixture is rinsed with boiling water into a flask having a mark at 200.3 c.c., and gradually made up to about 1 c.c. above the mark, some absolute alcohol being added during this operation whilst the flask is continuously shaken. The whole is allowed to digest for half an hour in the water-bath at 75°-80°, and, after cooling, made up to the mark. The flask is allowed to stand for half an hour if the pulp employed has been finely ground, or for two hours in the case of coarse pulp (with frequent shaking), and the solution is then filtered.

(c) **The Cold Aqueous Digestion Method.**—The modification of Pellet's method of cold aqueous digestion, recommended by F. Sachs,² which is an improvement on that of Kaiser and Lewenberg,³ has proved the most satisfactory. Le Docte has described an apparatus with which a large number of beetroot analyses may be very expeditiously carried out. The normal weight (26 g.) of fine beetroot pulp prepared with Pellet's "Sans Pareil" press⁴ or Herles apparatus or the Keil-Dolle mill (which must not make more than two hundred and fifty revolutions per minute⁵) is introduced into a cylindrical flat-bottomed dish of polished tinned copper; 177 c.c. of water containing 5 c.c. of basic lead acetate solution (or the water and basic lead acetate solution may be mixed beforehand in the proportion 30-35:1) are added, with stirring. After covering the dish with a greased glass plate covered with rubber, it is held with both hands (the thumbs keeping the glass plate in position) and shaken. Extraction is complete within three minutes, and the solution is filtered and the rotation of the filtrate determined (after addition of 2 drops of acetic acid if necessary) in a 400 mm. tube. According to Herzfeld,⁶ however, it is better to allow the dish to stand for thirty minutes with frequent stirring and shaking, to insure complete removal of the air; this removal of air is especially important in the case of beetroots that have undergone any change or have been frozen; it may also be effected by means of an air-pump.⁷

¹ *Z. Ver. deut. Zuckerind.*, 1909, 59, 627.

² *Bull. Assoc. Chim. Sucr.*, 1896, 14, 377; *Z. Ver. deut. Zuckerind.*, 1896, 46, 865.

³ *Deutsche Zuckerindustrie*, 1893, p. 413.

⁴ Concerning the special precautions to be observed in using the "Sans Pareil" press, cf. Le Docte, *Sucrierie Belge*, 1910, 39, 26.

⁵ Pellet, *Bull. Assoc. Chim. Sucr.*, 1904, 22, 317.

⁶ *Z. Ver. deut. Zuckerind.*, 1902, 52, 941.

⁷ Laszewski, *Zentralbl. für die Zuckerindustrie*, 1904, p. 283; *Bull. Assoc. Chim. Sucr.*, 1905, 22, 584; see, on the other hand, Pellet, *ibid.*, pp. 579 and 754.

A modified method of cold aqueous digestion which is very expeditious and trustworthy and also allows of the use of coarser pulp has been proposed by Herzfeld.¹ For the carrying out a large number of estimations rapidly a sufficient number of nickel-plated iron beakers and of weighing dishes of equal weights are required; the beakers are slightly constricted at the top, which is 4 cm. in diameter, and are stoppered with corks coated with tinfoil, whilst the dishes are of such size and shape as to permit of the ready transference of 26 g. of pulp to the beakers. This quantity of pulp is transferred to the beaker with exactly 177 c.c. (the quantity prescribed by Sachs) of a mixture of 200 parts of water and 5 parts of basic lead acetate solution delivered from an automatic burette. The beaker is then stoppered and thoroughly shaken, and, if the pulp employed be very finely divided and homogeneous, the solution may be filtered and the rotation of the filtrate determined at once. If, however, the pulp employed is coarse, the loosely stoppered beakers are placed for thirty minutes in a water-bath heated to 75°-80°, cooled to the room temperature and shaken, the rotation of the solution being determined in the usual way. The results generally agree with those obtained by the Sachs-Le Docte method, but sometimes they are higher by 0.2-0.4 per cent. In such cases, the extraction is evidently more complete, as is shown by the very valuable control method of alcoholic extraction.

In place of Herzfeld's beakers, Stanek and Urban² use a galvanised miniature milk can of 500 c.c. capacity, suitably covered, into which 52 g. of pulp are weighed and treated with 354 c.c. of water containing the requisite quantity of basic lead acetate.

Simultaneously with Herzfeld, Le Docte³ proposed a further modification of the original method of cold aqueous digestion, though this modified method is in no sense one of cold digestion. The beetroot slices are disintegrated with an improved meat-mincing machine having a screw of very short pitch. Six of the metal beakers, each containing the requisite quantities of pulp, water, and basic lead acetate, are suspended through a suitably perforated cover in a water-bath and kept at a temperature of 80°-85° for thirty minutes. The beakers are then immersed in a cold water-bath for ten minutes, after which the analysis is completed as before. Once everything is in working order the method can be carried out very rapidly and conveniently, and it is very useful for the execution of a large number of analyses daily. It is essential that the apparatus employed should be specially adapted to the purposes required; this apparatus includes an improved burette fitted with a four-way cock, for addition of water alone or of mixtures

¹ *Z. Ver. deut. Zuckerind.*, 1909, 59, 627.

² *Z. Zuckerind. Böhm.*, 1910, 34, 625.

³ *Sucrierie Belge*, 1909, 37, 530, 563; 1910, 38, 568.

of water and basic lead acetate solution in variable proportions which can be automatically controlled.

With careful work, Pellet's methods, and especially that of hot aqueous digestion, give satisfactory results agreeing with those obtained by alcoholic extraction, at least in the large majority of cases where normal beetroots (*i.e.*, beetroots grown and stored under favourable conditions) are examined; as Stift¹ has pointed out, however, perfectly concordant results are not to be expected. In the case of beetroots grown, harvested, or stored under abnormal conditions (*e.g.* beetroots containing much pectin substances) or of diseased beetroots (such cannot be detected by superficial inspection), the results obtained by Pellet's methods may, according to various observers, differ very appreciably from those obtained by alcoholic extraction.² Hence the latter method as a means of regular control is to be preferred in all doubtful cases, especially when the analytical results are to constitute the basis of manufacturing operations.

Where a large number of analyses are required, *e.g.* for the commercial valuation of the roots, or in the case of beetroot for seeds, in which cases comparative values only, and not absolutely accurate results are required, the cold aqueous digestion method is specially suitable. For the estimation of sucrose in seed beetroots only a small part of the root should be taken for analysis (in order that its subsequent growth may not be affected); for this purpose, Keil and Dolle's seed beetroot boring machine is used. The quarter normal weight of pulp, and a pipette of 44.25 c.c. capacity are employed, the method being carried out as described under (c). Pellet's continuous tube, which can be filled with solution without removing the cap, may be used for the polarisation readings.³

For a large number of analyses, a very handy apparatus, constructed by Krüger⁴ and supplied by Primavesi of Magdeburg, is much used, although the results obtained are often very appreciably lower than those obtained by the method of Sachs-Le Docte or of Herzfeld.

According to Frühling,⁵ Krüger's apparatus is best used in an improved form, in which a pipette is used which is fitted with only one glass stopcock, which can easily be cleaned and inserted again at any time. A counterpoise, corresponding to the weight of pulp (which may be 5-50 g.) that the pipette is intended to contain, is supplied with each pipette, and under the conditions prescribed the polarimetric reading gives the percentage of sucrose in the beetroot directly.

¹ *Oesterr.-Ungar. Zeitschr.*, 1901, 29, 411.

² *Cf. Strohmer, Oesterr.-Ungar. Zeitschr.*, 1910, 39, 656.

³ *Z. Ver. deut. Zuckerind.*, 1891, 41, 338; 1892, 42, 377.

⁴ *Deutsche Zuckerindustrie*, 1896, p. 2434; improved construction, *ibid.*, 1904, p. 1644.

⁵ *Deutsche Zuckerindustrie*, 1904, p. 1545. The apparatus and directions for use may be obtained from the laboratory of Frühling and Schulz, Brunswick.

B.—ESTIMATION OF FIBRE OR JUICE AND OF DRY SUBSTANCE.

By the term "Fibre" of the beetroot is understood the solid constituents of the root insoluble in water, which in the dry state generally amount to 4-5 per cent. of the weight of the root. The content of fibre is determined by complete extraction of 20 g. of extremely fine shavings or fine pulp which are treated with about 400 c.c. of water in a beaker and allowed to stand, with stirring, for half an hour. The supernatant liquor is then removed, best by means of a filter-pump, in which case a glass tube, funnel-shaped at its lower end, and provided with a closely fitting wad of pianoforte felt at the apex of the funnel (15 mm. wide), is immersed in the solution. As soon as the residue in the beaker appears sufficiently free from water, fresh water is added, the operation being repeated until no soluble matter is left in the residue. Finally, the residue is placed on a previously dried and weighed filter, the wad thoroughly rinsed, and the residue washed successively with hot water, alcohol, and ether. The filter and contents are then dried, first at a moderate temperature (50°-60°), then at 100°-105° (or at most 110°), and finally weighed and incinerated.

Skärblom¹ has proposed the following method of estimation:— 10 g. of the finely divided sample and 40 c.c. of cold water are thoroughly mixed with a glass rod. The mixture is rinsed on to a weighed small glass funnel fitted with a finely perforated platinum cone, washed with boiling water until a 200 c.c. flask is filled with the filtrate (the last portion of which should not give the reaction for sugar with α -naphthol). The fibre is then carefully pressed down in the funnel, treated with 20 c.c. of 95 per cent. alcohol, freed from liquid by suction, and then dried until its weight is constant, which can be effected in one to two hours.

The weight of ash is deducted from the total dry residue and the remainder is taken to represent ash-free fibre; the difference between this amount and 100 gives the so-called "juice-content," a value which does not, however, possess the significance that many have ascribed to it. For, since the solubility of the solid constituents depends to a great extent on their nature, on the kind of extracting liquid, on the temperature, etc., and since further the fibre is not contained in the beetroot as such, *i.e.* anhydrous, it is evident that the percentage of dry fibre depends on many contingencies, and that no trustworthy conclusions concerning the actual amount of juice in the root can be deduced from it. Hence, for the purposes of manufacturing control the so-called juice-content must never be taken as a guide, but only the percentage of sucrose in the beetroot.

¹ *Z. Ver. deut. Zuckerind.*, 1910, 60, 931.

The drying ovens¹ used for the estimation of water in all the raw materials and products connected with sugar manufacture must be so constructed that the temperature indicated by the thermometer is actually the temperature of the oven. Air drying ovens with single walls and direct heating of the bottom are to be condemned; such as are provided with double walls and proper air circulation are, however, admissible. The dishes containing the substances to be dried are placed on asbestos cards in order to avoid direct heat conduction. Drying ovens, the interior of which is maintained at the requisite temperature by means of suitable vapours or liquids (toluene, glycerol) circulating between double walls, guarantee absolute certainty against overheating. A convenient form of drying oven has been devised by R. L. Siau.² Baumann and Horn's vacuum drying oven³ may also be specially commended. Vacuum drying ovens are quite indispensable if the substances under examination are of an acid nature or if they contain considerable quantities of invert sugar, since otherwise decomposition occurs during the heating in presence of air, and a constant weight cannot generally be obtained. If a vacuum drying oven is not available, such materials are best dried with the help of a current of an indifferent gas such as hydrogen or carbon dioxide.⁴

Glass or nickel dishes about 7 cm. in diameter and 2 cm. in height form suitable receptacles for the substance to be dried; in the case of hygroscopic substances, the dishes must be provided with an overlapping cover and handle.

In order to obtain a mass with a large surface, fluid or semi-fluid substances are best intimately mixed with a sufficient quantity of pure ignited quartz sand free from iron, from which the dust has been removed by careful sifting. The mixing should be effected with a glass rod forming part of the tare, and the mixture should form a loose friable mass. Dilute solutions are first evaporated to a syrupy consistency on the water-bath, and then, after admixture with sand, dried until the weight is constant.

To estimate the percentage of dry substance in the beetroot according to Claassen's method, 20-25 g. of the pulp (prepared with a mincing machine and thoroughly mixed) are weighed out as rapidly as possible into a shallow glass dish of 8 cm. diameter, together with a glass rod. The pulp is spread out well, dried for two hours at 70°, thoroughly stirred and pressed, spread out again, and then dried

¹ Cf. Soxhlet, *Z. Ver. deut. Zuckerind.*, 1891, 41, 691; Alberti and Hempel, *Deutsche Zuckerindustrie*, 1892, p. 385; *Z. Ver. deut. Zuckerind.*, 1892, 42, 856; 1893, 43, 130, 445.

² *J. Soc. Chem. Ind.*, 1911, 30, 61.

³ *Korrespondenzblatt*, 1894, No. 18.

⁴ Cf. Drenckmann, *Zentralbl. für die Zuckerindustrie*, 1897, p. 1107; and Geese, *ibid.*, 1904, p. 778.

in vacuo at 106° - 108° until the weight is constant, this being effected in about eight hours; on further drying (for two to three hours), the loss in weight should not exceed, at most, 10 mg.¹

Skärblom² found that addition of sand is unnecessary, and considers also that the preliminary drying can be dispensed with provided that the drying process is effected *in vacuo*.

C.—ESTIMATION OF INVERT SUGAR.

The estimation of invert sugar in the beetroot is based upon the methods commonly used for estimating invert sugar in the products of sugar manufacture.

As is well known, the direct polarimetric reading of substances containing sucrose does not represent the true percentage of sucrose if other optically active substances are also present. In the case of invert sugar, for instance, 1 part of this substance counteracts the optical activity of about 0.34 parts of sucrose. Since, however, the value of this factor varies according to the way in which the product has been treated during manufacture, it is inadmissible to make a correction by multiplying the percentage of invert sugar by 0.34 and adding the product thus obtained to the direct polarimetric reading; on this account, the content of invert sugar found by direct determination is always stated apart from the polarimetric reading.³

As a rule, in practice, the detection and estimation of invert sugar is based on the fact that sugars of this kind possess the property of reducing solutions of cupric salts containing alkali when boiled therewith, whereby the copper is precipitated in the form of red cuprous oxide. The amount of copper reduced by a given weight of invert sugar is, however, not constant under all conditions, but is dependent on the composition of the copper solution, on the concentration of the sugar solution, on the relative quantities of these solutions, on the duration of the reaction, and also on the way in which the determination is carried out. In other words, the cupric reduction method is empirical. Hence, to obtain accurate and comparable results the experimental conditions prescribed must be strictly observed.

The qualitative test for invert sugar is carried out under conditions similar to those for quantitative estimation. If no cuprous oxide is precipitated or a quantity too small to weigh, no further examination is needed; otherwise, a quantitative estimation must be made. For qualitative purposes it is sufficient to boil about 10 drops of a concentrated solution of the sample to be examined with about 15 c.c. of Fehling's solution in a test tube. In carrying out the test, various

¹ *Z. Ver. deut. Zuckerind.*, 1910, 60, 323.

² *Ibid.*, 1910, 60, 931.

³ Cf. Lippmann, *Chemie der Zuckerarten*, p. 1420.

conditions, which may cause decomposition or secondary reactions, and hence may lead to error, must be guarded against.¹ The sugar and copper solutions must be thoroughly mixed and the mixture must be uniformly heated; moreover the boiling must be neither too vigorous nor too prolonged.

The estimation may be carried out either gravimetrically or volumetrically.

For the first method Tables have been prepared for various relative proportions of sucrose and invert sugar from which the amount of invert sugar corresponding to a given quantity of copper can be found.

The estimation of sucrose by inversion may be carried out by the cupric reduction method, and is specially applicable when a large proportion of invert sugar is present.

The Fehling's solution used for the estimation of invert sugar is prepared, according to Soxhlet's² method, as follows:—

I. 34.639 g. of crystallised, chemically pure copper sulphate are dissolved and made up to 500 c.c. with pure distilled water.

II. 173 g. of crystallised, purest Rochelle salt are dissolved in nearly 400 c.c. of pure distilled water, and to the solution are added 100 c.c. of a sodium hydroxide solution containing 516 g. of purest sodium hydroxide per litre; the whole is then made up to 500 c.c.

For use, equal volumes of the perfectly clear solutions I. and II. are mixed together; the mixture should not be kept for more than a day.

(a) Gravimetric Estimation of small quantities of Invert Sugar (0.05-1 per cent.) in presence of Sucrose.

For this purpose, Herzfeld³ has compiled a Table by which the percentage of invert sugar in the substance may be found directly from the weight of copper obtained by reduction, on the assumption that 10 g. of the substance are dissolved to 50 c.c. and that the time of boiling is exactly two minutes. The sugar solution must always be perfectly clear; in the case of comparatively pure samples, a solution containing 20 g. in 100 c.c. is used and 50 c.c. of the filtrate are taken for the estimation; in all other cases 25 g. of the substance are dissolved in water, and after addition of basic lead acetate solution, made up to 100 c.c. and filtered. 60 c.c. of the filtrate are freed from lead by addition of sodium carbonate, made up to 75 c.c. and filtered, 50 c.c. of the filtrate (containing 10 g. of the substance) being used for estimation.

¹ Cf. Lippmann, *Chemie der Zuckerarten*, p. 1396.

² *Neue Zeitschr. f. Rübenzuck.-Ind.*, 1880, p. 141.

³ *Z. Ver. deut. Zuckerind.*, 1885, 35, 967; 1886, 56, 278; 1890, 40, 447.

The 50 c.c. of solution are thoroughly mixed with 50 c.c. of freshly prepared Fehling-Soxhlet solution in an Erlenmeyer boiling flask of about 300 c.c. capacity, and then placed on an asbestos-covered wire gauze with a circular opening, and heated to boiling as quickly as possible (within three to four minutes) with a good triple burner. As soon as the boiling point is reached, *i.e.* when bubbles begin to rise from all parts of the solution, the contents of the flask are kept at the boil for exactly two minutes by means of the smaller flame of a single burner. The solution is then mixed at once with 100 c.c. of cold, distilled water, free from air, in order that it may be cooled and the further precipitation of cuprous oxide thus prevented, and finally filtered by suction through a previously weighed Soxhlet tube. This is a thick-walled tube of hard glass, about 2 cm. in diameter and 12-14 cm. long, one end of which is drawn out to a conical shape. At the constriction of the tube is placed a perforated platinum cone, and on the latter a layer of purest, specially prepared asbestos,¹ about 2 cm. deep and uniformly pressed down. The asbestos, after being washed with hot water, is washed with alcohol and then with ether, and finally ignited in a current of air, and allowed to cool in a desiccator. Soxhlet tubes that have been used are treated with a few drops of fuming nitric acid to dissolve the copper, which is then washed out with hot water, alcohol, and ether, and finally the tube is dried and ignited. When the weight of the tube no longer remains constant it must be replaced by a new one.

Before filtration, the Soxhlet tube, which is fitted to a filter flask, is provided with a small funnel; the funnel and tube are first moistened with water, and then the copper solution is filtered off, with the aid of the pump. Care must be taken that during the whole time of filtration the Soxhlet tube is never allowed to get quite empty. The precipitate is best washed into the tube with cold water to prevent it, as far as possible, from adhering to the sides of the tube. It is then washed successively with 300-400 c.c. of boiling water and 20 c.c. of absolute alcohol, and dried in an oven at 130°-200°; finally, the tube is heated to dull redness at the part where the asbestos is placed, in order to convert the cuprous into cupric oxide, and at the same time to destroy the small quantities of organic copper compounds that are sometimes present. The tube is then connected to a hydrogen generator, and the copper oxide reduced to metallic copper by careful heating to dull redness. This operation is finished in a few minutes. As soon as the water formed by the reduction is driven off, the tube is allowed to cool in a current of hydrogen, and then weighed immediately.

Instead of an asbestos filter, a suitable paper filter may be used. In this case the precipitate is washed first with cold water, then with 300-

¹ Fresenius, *Z. anal. Chem.*, 1883, 22, 552; *Z. Ver. deut. Zuckerind.*, 1897, 47, 1077.

400 c.c. of hot water, the filter and precipitate incinerated, and reduced in a platinum crucible covered with a perforated porcelain lid.

According to Andrlik and Hranicka¹ as well as Bruhns² the copper oxide ignited in the dish may be reduced by means of methyl or ethyl alcohol vapour. For the details of this method, which has been proved satisfactory by other investigators,³ the original papers must be consulted.

It is also permissible to omit the reduction to metallic copper, and to convert the cuprous oxide into cupric oxide by ignition, and weigh

Table 41.

For calculating the Percentage of Invert Sugar in the presence of Sucrose from the weight of Copper obtained, 10 g. of substance being used.⁴

Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
50	0.05	120	0.40	190	0.79	260	1.19
55	0.07	125	0.43	195	0.82	265	1.21
60	0.09	130	0.45	200	0.85	270	1.24
65	0.11	135	0.48	205	0.88	275	1.27
70	0.14	140	0.51	210	0.90	280	1.30
75	0.16	145	0.53	215	0.93	285	1.33
80	0.19	150	0.56	220	0.96	290	1.36
85	0.21	155	0.59	225	0.99	295	1.38
90	0.24	160	0.62	230	1.02	300	1.41
95	0.27	165	0.65	235	1.05	305	1.44
100	0.30	170	0.68	240	1.07	310	1.47
105	0.32	175	0.71	245	1.10	315	1.50
110	0.35	180	0.74	250	1.13		
115	0.38	185	0.76	255	1.16		

the latter as such. The conversion into cupric oxide may be effected in a Soxhlet tube,⁵ or more easily in an open platinum dish, but it is necessary to observe certain precautionary measures.⁶ In using Table 41 the weight of copper must then of course be calculated from the weight of copper oxide found. The direct weighing of the cuprous oxide is only permissible when the sugar solutions under examination are pure or nearly so.⁷ Ling and B. F. Davies⁸ have shown that,

¹ *Z. Ver. deut. Zuckerind.*, 1897, 47, 1077.

² *Zentralbl. für die Zuckerindustrie*, 1897, p. 44.

³ Cf. Lippmann, *Chemie der Zuckerarten*, p. 595.

⁴ *Z. Ver. deut. Zuckerind.*, 1885, 35, 1012.

⁵ Farnsteiner, *Z. Ver. deut. Zuckerind.*, 1895, 45, 844.

⁶ Cf. Lippmann, *Chemie der Zuckerarten*, p. 596 ff.

⁷ Cf. C. O'Sullivan and A. L. Stern, *J. Chem. Soc.*, 1896, 69, 1692.

⁸ *J. Inst. Brewing*, 1902, 8, 477.

when pure solutions of reducing sugars are being dealt with, the cuprous oxide may be collected in a Gooch crucible and dried and weighed as such. With impure sugar solutions the results may be too high by 0.25-0.50 per cent. according to C. A. Browne,¹ owing to precipitation of foreign substances.

Many sugar products, especially syrups and molasses, give precipitates of green copper compounds when 10 g. of the material are taken for analysis, a factor which renders the estimation of invert

Table 42.

For calculating the Percentage of Invert Sugar in the presence of Sucrose from the weight of Copper obtained, 5 g. of substance being used. (Baumann.)²

Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
(35)	(0.04)	110	0.83	185	1.65	260	2.50
40	0.09	115	0.88	190	1.70	265	2.56
45	0.14	120	0.93	195	1.76	270	2.62
50	0.19	125	0.99	200	1.82	275	2.68
55	0.25	130	1.04	205	1.87	280	2.74
60	0.30	135	1.10	210	1.93	285	2.79
65	0.35	140	1.15	215	1.98	290	2.85
70	0.40	145	1.21	220	2.04	295	2.91
75	0.45	150	1.26	225	2.10	300	2.97
80	0.51	155	1.31	230	2.16	305	3.03
85	0.56	160	1.37	235	2.21	310	3.09
90	0.61	165	1.42	240	2.27	315	3.15
95	0.66	170	1.48	245	2.33	320	3.21
100	0.72	175	1.54	250	2.39		
105	0.77	180	1.59	255	2.44		

sugar by the usual method impossible. In such cases a solution of 5 g. of the sample in 50 c.c. is used for the estimation.³ The results are found from Table 42 (Baumann),⁴ the actual analysis being carried out exactly according to Herzfeld's method.

(b) Gravimetric Estimation of larger quantities of Invert Sugar in the presence of Sucrose.

For the determination of larger quantities of invert sugar a Table of factors was first compiled by E. Meissl,⁵ which was afterwards amplified by E. Hiller.⁶ According to the original method, the

¹ *Int. Sugar J.*, 1908, 10, 537.

² *Z. Ver. deut. Zuckerind.*, 1890, 40, 778.

³ *Ibid.*, 1909, 59, 487.

⁵ *Ibid.*, 1883, 33, 765.

⁴ *Ibid.*, 1892, 42, 825.

⁶ *Ibid.*, 1889, 39, 734.

normal weight of the substance is dissolved in water, clarified with basic lead acetate, made up to 100 c.c., filtered, and the rotation determined in a 200 mm. tube. The excess of lead is removed from an aliquot part of the filtrate with the requisite quantity of sodium carbonate solution, the whole being made up to a known volume and filtered; 50 c.c. of the filtrate are used for the estimation of invert sugar according to the usual method. The solution should be of such dilution that 100-200 mg. of invert sugar, corresponding to 200-400 mg. of copper, are contained in the 50 c.c. of solution used for the estimation. According to Schrefeld,¹ however, the clarification of solutions containing invert sugar with basic lead acetate causes a considerable decrease of the reducing power under certain circumstances; this decrease is generally more marked as the content of invert sugar increases and the purity of the substance decreases. Hence, in the analysis of crude syrups and molasses it is best to use normal lead acetate instead of the basic acetate.

The following is a simpler method in which, however, clarification with basic lead acetate must be avoided:—10 g. of the substance under examination are dissolved in water and made up to 100 c.c. Into each of several test-tubes 5 c.c. of Fehling's solution and various quantities of the sugar solution (*e.g.* 8 c.c. in the first, 6 c.c. in the second, 4 c.c. in the third, and 2 c.c. in the last tube) are introduced. The contents of the tubes are then boiled, and the quantity of substance to be used in the subsequent quantitative analysis is indicated by that tube the contents of which still show a blue colour after boiling. Thus, if the tube containing 6 c.c. of sugar solution is the last of the series still showing a blue colour, 6 g. of the substance are weighed out, dissolved in water, and made up to 50 c.c. without addition of basic lead acetate; the solution is then boiled with 50 c.c. of Fehling's solution for two minutes, and further treated as in (a).

If, in the above method, it is desired to clarify the solution with basic lead acetate, the following procedure is to be recommended:—27.5 g. of the substance are dissolved in a 125 c.c. flask, the solution clarified with basic lead acetate or lead acetate, made up to the mark with water, mixed, and filtered. According to the result of the preliminary test described above, 80, 60, 40, 20, or 10 c.c. of the solution (containing 17.6, 13.2, 8.8, 4.4, or 2.2 g. of substance) are measured with a pipette into a flask graduated to 100 and 110 c.c., made up to the first mark with water, and to the second with a solution of sodium carbonate (30 parts of crystallised sodium carbonate dissolved in 100 parts of water); the solution is then mixed and filtered. 50 c.c. of this filtrate (containing 8, 6, 4, 2, or 1 g. of substance, according to the amount of solution originally taken) are then boiled for two

¹ *Z. Ver. deut. Zuckerind.*, 1908, 58, 947.

minutes with 50 c.c. of Fehling's solution in the usual way, a certain quantity of copper being thus obtained.

The calculation of the result is made as follows:—Let P = the polarisation reading of the substance, and p = the amount of substance used for the determination of invert sugar which has given Cu grams of copper. The amount of invert sugar, A , contained in p grams is approximately equal to $Cu/2$.

Table 43.

Table giving the Factors to be used in Calculations for the Determination of Invert Sugar in presence of Sucrose.¹ (E. Hiller.)

Invert sugar in 100 parts of total sugar = B.	Milligrams of invert sugar = A.						
	200	175	150	125	100	75	50
100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

From the equation:—

$$\left(A + \frac{p \times P}{100}\right) : A = 100 : B,$$

the value of B may be found, which represents the quantity of invert sugar contained in 100 parts of the mixture of sucrose + invert sugar. The percentage of invert sugar in the substance is found from the equation:—

$$\frac{Cu}{p} \times F = \text{Percentage of Invert Sugar},$$

in which p represents the amount of substance employed and F a factor to be taken from Table 43. This factor is obtained from the

¹ The German Official Customs Method, 1896. Cf. *Z. Ver. deut. Zuckerind.*, 1889, 39, 735.

horizontal and vertical columns of the Table which correspond most closely to the values found for A and B. In the case of substances containing much invert sugar, it is better to determine the total content of sugar by inversion and gravimetric analysis (see under (c)) than to employ the polarimetric method.

(c) The Gravimetric Inversion Method.

In the presence of very large quantities of invert sugar, the total amount of sugar is estimated, after inversion, as invert sugar (inverted sucrose + invert sugar originally present), and from the amount of copper obtained the total sugar is calculated as sucrose. The invert sugar-content in the original substance estimated by a special experiment according to (b) is converted into the equivalent amount of sucrose by multiplying by 0.95 (since 95 parts by weight of sucrose give 100 parts by weight of invert sugar on inversion), and this value is subtracted from the total sugar-content; the difference gives the content of sucrose.

Provided that the method of working is exactly followed, Table 44, compiled by Herzfeld,¹ renders any calculation unnecessary, since it gives directly the percentage of total sugar calculated as sucrose, corresponding to the amount of copper found directly.

The analysis is carried out as follows:—For converting the sucrose into invert sugar, Herzfeld's inversion method² is employed. Half the normal weight of substance (13 g.) is dissolved in 75 c.c. of water in a 100 c.c. flask; 5 c.c. of hydrochloric acid of sp. gr. 1.19 are added, and the flask is then heated, with shaking, to 67° in about three minutes by immersion in a water-bath heated to 70°, and subsequently maintained for exactly five minutes at a temperature of 67°-70°. The flask is cooled immediately to 20°, its contents made up to 100 c.c., and 50 c.c. of the well-mixed and filtered liquid diluted to 1 litre with distilled water. After the diluted liquid has been thoroughly mixed, 25 c.c. (= 0.1625 g. of the original substance) are transferred to an Erlenmeyer flask. The free acid present is carefully neutralised by the gradual addition of 25 c.c. of a solution containing 1.7 g. of anhydrous sodium carbonate per litre, 50 c.c. of Fehling-Soxhlet's solution added, and the whole heated to boiling in the usual way, and maintained at the boiling point for three minutes. The further treatment of the precipitated cuprous oxide is exactly the same as in (a).

For example, by the above method 0.162 g. of copper were obtained, and in the invert sugar estimation, according to (b) by using 4.0 g. of substance, 0.310 g. of copper were obtained. From Table 44

¹ *Z. Ver. deut. Zuckerind.*, 1896, 46, 417.

² *Ibid.*, 1896, 46, 699.

Table 44.

For calculating the Percentage of Sucrose, corresponding to the Invert Sugar present, from the amount of Copper obtained, the duration of boiling being three minutes, and the amount of substance used being 0.1625 g.¹ (Herzfeld.)

Copper.	Sucrose.	Copper.	Sucrose.	Copper.	Sucrose.	Copper.	Sucrose.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
79	24.57	126	38.87	173	53.63	220	68.87
80	24.87	127	39.18	174	53.95	221	69.20
81	25.17	128	39.49	175	54.27	222	69.53
82	25.47	129	39.80	176	54.59	223	69.87
83	25.78	130	40.11	177	54.91	224	70.20
84	26.08	131	40.42	178	55.23	225	70.53
85	26.38	132	40.73	179	55.55	226	70.86
86	26.68	133	41.04	180	55.87	227	71.19
87	26.98	134	41.35	181	56.19	228	71.53
88	27.29	135	41.66	182	56.51	229	71.86
89	27.59	136	41.98	183	56.83	230	72.19
90	27.89	137	42.29	184	57.15	231	72.52
91	28.19	138	42.60	185	57.47	232	72.85
92	28.50	139	42.91	186	57.79	233	73.18
93	28.80	140	43.22	187	58.11	234	73.51
94	29.10	141	43.53	188	58.43	235	73.85
95	29.40	142	43.85	189	58.75	236	74.18
96	29.71	143	44.16	190	59.07	237	74.51
97	30.02	144	44.48	191	59.39	238	74.84
98	30.32	145	44.79	192	59.72	239	75.17
99	30.63	146	45.10	193	60.04	240	75.50
100	30.93	147	45.42	194	60.36	241	75.83
101	31.24	148	45.73	195	60.69	242	76.17
102	31.54	149	46.05	196	61.01	243	76.51
103	31.85	150	46.36	197	61.33	244	76.84
104	32.15	151	46.68	198	61.65	245	77.18
105	32.45	152	46.99	199	61.98	246	77.51
106	32.76	153	47.30	200	62.30	247	77.85
107	33.06	154	47.62	201	62.63	248	78.18
108	33.36	155	47.93	202	62.95	249	78.52
109	33.67	156	48.25	203	63.28	250	78.85
110	33.97	157	48.56	204	63.60	251	79.19
111	34.27	158	48.88	205	63.93	252	79.53
112	34.58	159	49.19	206	64.26	253	79.88
113	34.88	160	49.50	207	64.58	254	80.22
114	35.19	161	49.82	208	64.91	255	80.56
115	35.49	162	50.13	209	65.23	256	80.90
116	35.80	163	50.45	210	65.56	257	81.24
117	36.10	164	50.76	211	65.89	258	81.59
118	36.41	165	51.08	212	66.22	259	81.93
119	36.71	166	51.40	213	66.55	260	82.27
120	37.01	167	51.72	214	66.88	261	82.61
121	37.32	168	52.04	215	67.21	262	82.95
122	37.63	169	52.35	216	67.55	263	83.30
123	37.94	170	52.67	217	67.88	264	83.64
124	38.25	171	52.99	218	68.21	265	83.98
125	38.56	172	53.31	219	68.54	266	84.32

¹ The German Official Customs Method. *Loc. cit.*

it is found that for $\text{Cu} = 0.162$ g. the total sugar-content, calculated as sucrose, = 50.13 per cent. From Table 43 the factor 52.1 is found, hence $I = \frac{0.310 \times 52.1}{4} = 4.04$ per cent. of invert sugar. This

amount of invert sugar, reckoned as sucrose, is included in the figure 50.13 for the total sugar, and therefore, after multiplying by 0.95, must be subtracted from the total sugar. Consequently the percentage of sucrose = $50.13 - 3.84 = 46.29$ per cent.

(d) The Volumetric Estimation of Invert Sugar.

Since the degree of reduction of the Fehling-Soxhlet solution is dependent on the concentration, and every value obtained is only valid for the concentration at which it is determined, it is necessary, in order to obtain accurate results, to work under approximately the same conditions of concentration. According to Soxhlet¹ 50 c.c. of Fehling's solution are heated to boiling in a deep porcelain dish, portions of the sugar solution being added from time to time, until the liquid, after boiling for two minutes, no longer appears blue. When the amount of invert sugar in the solution has been roughly determined, by this preliminary test, the solution is diluted so as to contain 1 per cent. of invert sugar. 50 c.c. of undiluted Fehling's solution are heated to boiling, and as much of the 1 per cent. solution of invert sugar is added as is required (according to the preliminary test) to decolorise the solution completely; the whole is then boiled for two minutes and filtered through a pleated filter. The filtrate is examined for copper unless it is distinctly blue or greenish in colour. This is done by acidifying with acetic acid and adding a few drops of a solution of potassium ferrocyanide. The presence of a considerable quantity of copper is indicated by a dark red coloration; traces of copper give a rose colour; if no colour is obtained, all the copper has been reduced and an excess of sugar is present. If copper is found to be present, a second estimation is made with more sugar solution; if no copper is found, a smaller quantity of sugar solution is used and the titrations are repeated (generally five or six times) until of two determinations with which the quantities of sugar solution only differ by 0.1 c.c., one gives a copper-containing filtrate and the other a filtrate free from copper, the mean value being taken as the result. According to Soxhlet 50 c.c. of Fehling's solution corresponds to 0.2470 g. of invert sugar in 1 per cent. solution with a period of boiling of two minutes.

In the case of coloured solutions, the filtrate is boiled with a few drops of the sugar solution for one minute and allowed to stand for three or four minutes; the solution is then poured off and the bottom

¹ *J. prakt. Chem.*, 1880 [2], 21, 227.

of the flask is wiped with a soft filter paper wrapped round a glass rod; even very small quantities of cuprous oxide colour the paper red. The results of this volumetric method are accurate to within at least 2 per cent.

In order to ensure accurate results it is advisable to standardise the copper solution, for which purpose a solution of pure invert sugar of known concentration is used. To obtain the latter, 9.5 g. of absolutely pure sucrose are hydrolysed in a 100 c.c. flask according to Herzfeld's inversion method described above; after the solution, which now contains 10 g. of invert sugar, has been made up to the mark and thoroughly mixed, 20 c.c. of it (= 2.0 g. of invert sugar) are transferred by means of a pipette to a litre flask, exactly neutralised with a dilute solution of sodium carbonate, and made up to the mark. In this way a 0.2 per cent. solution of invert sugar is obtained which is titrated by the method described above.

In the volumetric estimation of invert sugar, the use of potassium ferrocyanide as indicator has the disadvantage that a portion of the assay liquid must be filtered for each test; again, when certain amino-compounds are present in the liquid, so much cuprous oxide may be dissolved that it is impossible to obtain an acidified filtrate which gives no colour with potassium ferrocyanide. For these reasons Ling and Rendle,¹ and Ling and Jones² recommend the use of ferrous thiocyanate instead of potassium ferrocyanide as an indicator for the unreduced copper; in presence of cupric salt, the ferrous thiocyanate is oxidised to the red ferric compound. With this indicator there is no necessity to filter off a portion of the assay liquid. To prepare the indicator, 1 g. of ferrous ammonium sulphate and 1.5 g. of ammonium thiocyanate are dissolved in 10 c.c. of water at, say, 45°-50°, the solution being cooled at once and treated with 2.5 c.c. of concentrated hydrochloric acid. The solution thus obtained has a brownish red colour (due to ferric salt) which is removed by adding a trace of zinc dust; the red colour reappears in the course of some hours, but may be destroyed again by the addition of a further quantity of zinc dust, though the delicacy of the indicator is impaired after several decolorisations. The method of titration is as follows:—10 c.c. of *undiluted* Fehling's solution is heated to boiling, the sugar solution (which should be adjusted to such a concentration that 20-30 c.c. are required for titration) then being run into the boiling liquid in small amounts beginning with 5 c.c. After each addition of sugar solution the mixture is boiled, the liquid being kept in rotation. About 12 drops of the indicator are placed on a porcelain slab, and when it is judged that the precipitation of cuprous oxide is complete, a drop of the assay liquid is withdrawn with a glass rod and brought into contact rapidly with the indicator on the slab.

¹ *Analyst*, 1905, 30, 182.

² *Ibid.*, 1908, 33, 160.

The titration must be carried out rapidly, since an atmosphere of steam is then kept in the neck of the flask and the influence of atmospheric oxygen is avoided. At the final point, the liquid is boiled for about ten seconds. The Fehling's solution should be standardised against a 0.2 per cent. solution of invert sugar prepared as follows:—Pure sucrose (0.95 g.) is dissolved in water (150 c.c.) and boiled with $N/2$ hydrochloric acid (30 c.c.), the mixture being maintained in ebullition for one minute, cooled, neutralised by the addition of $N/2$ sodium

Table 45.

Table for correcting the Percentage of Invert Sugar for the contained Sucrose as determined by Ling's Method. (Ling and Rendle.)

A.	B.	C.	D.	E.	F.
...	...	100.0	25.65
0.01	4.8	95.2	25.60	95.30	0.10
0.03	13.0	87.0	25.60	87.10	0.10
0.05	20.0	80.0	25.60	80.10	0.10
0.10	33.3	66.7	25.55	66.90	0.20
0.20	50.0	50.0	25.45	50.40	0.40
0.30	60.0	40.0	25.40	40.40	0.40
0.40	66.6	33.4	25.35	33.80	0.40
0.50	71.4	28.6	25.30	29.00	0.40
0.60	75.0	25.0	25.20	25.40	0.40
0.70	77.7	22.3	25.15	22.70	0.40
0.80	80.0	20.0	25.10	20.40	0.40
1.25	86.2	13.8	25.05	14.10	0.30
1.50	88.2	11.8	24.95	12.10	0.30
1.75	89.7	10.3	24.85	10.60	0.30
2.00	90.9	9.1	24.80	9.40	0.30
2.50	92.5	7.5	24.80	7.76	0.26
3.00	93.8	6.2	24.70	6.44	0.24
5.00	96.1	3.9	24.20	4.13	0.23
7.00	97.2	2.8	23.60	3.04	0.24
10.00	98.0	2.0	22.95	2.23	0.23
20.00	99.0	1.0	22.40	1.14	0.14
25.00	99.2	0.8	22.25	0.92	0.12
30.00	99.3	0.7	22.25	0.80	0.10

hydroxide (30 c.c.), and made up with water to 500 c.c. This solution, which contains 0.2 g. of invert sugar per 100 c.c., is titrated with 10 c.c. portions of Fehling's solution as described above. If the solution under examination be diluted to such a degree that its content of invert sugar, roughly estimated in a preliminary experiment, approximates to 0.2 per cent., the true content of invert sugar may then be estimated quite as accurately as by the gravimetric method. Sucrose when present has some influence on the results, and to correct the percentage of invert sugar as found by the

above-described method, Ling and Rendle¹ have compiled Table 45, in which :—

Column A gives the amount in grams of sucrose in 100 c.c. of the sugar solution.

Column B gives the percentage of sucrose expressed on the total sugars.

Column C gives the percentage of invert sugar expressed on the total sugars.

Column D gives the number of cubic centimetres of sugar solution required to reduce 10 c.c. of Fehling's solution.

Column E gives the percentage of invert sugar on the total sugars found by direct experiment.

Column F gives the differences between the values given in Columns C and E.

The Estimation of Invert Sugar in Beetroot.—The following method of Claassen² for estimating invert sugar in beetroot is founded on the method given under (d):—110 g. of finely chopped or ground slices or beetroot pulp is digested in a $\frac{1}{2}$ -litre flask for about an hour on the water-bath with water, 10-15 c.c. of basic lead acetate solution and 2 g. of precipitated calcium carbonate being added. After cooling and filling to the mark, the moderately clear and only slightly acid juice is decanted off, 100 c.c. of the solution, treated with sufficient basic lead acetate to ensure complete clarification, made up to 110 c.c. with water, and filtered; 100 c.c. of the filtrate are then treated with a quantity of sodium carbonate solution sufficient to precipitate the lead, and made up to 200 c.c. with water and again filtered. Of this filtrate 100 c.c., containing the reducing sugar from 10 g. of beetroot, is used for titration. In the first place the titre of the Fehling's solution is determined; this is done by adding to 10 c.c. of boiling Fehling's solution a 0.2 per cent. solution of invert sugar (prepared as described above) together with 1.5 g. of sucrose (the average amount of sucrose in 10 g. of beetroot) until the test with potassium ferrocyanide shows that reduction is complete.

For the actual analysis, 100 c.c. of the solution (see above) are maintained at the boiling temperature with 10 c.c. of Fehling's solution for two minutes, and then titrated with the invert sugar solution above mentioned until the filtrate, on treatment with acetic acid and potassium ferrocyanide, no longer gives the copper reaction. For this test, the drop reaction papers made by Schleicher and Schüll are most suitable. The difference between the number of cubic centimetres of the solution of invert sugar used in the preliminary titration, and in the actual analysis, multiplied by 0.002, gives the amount of invert sugar in

¹ *Analyst*, 1908, 33, 169.

² *Deutsche Zuckerindustrie*, 1893, p. 337; and, *Zentralbl. Zuckerind.*, 1896, No. 83.

10 g. of the beetroot, and the latter, multiplied by 10, gives the percentage.¹

To ascertain whether the amount of invert sugar in the beetroot is sufficient to require a quantitative determination, the following method, proposed by Herzfeld,² is used:—20 c.c. of the solution prepared for the determination of sugar polarimetrically is mixed in a test tube with 0.5 c.c. of Fehling's solution and boiled for two minutes. If, now, the filtered solution is still blue, or if, after being cooled, freed from lead by addition of a few drops of sodium carbonate solution, and filtered again, it shows the reaction for copper on addition of acetic acid and potassium ferrocyanide, it may be concluded that the sample does not contain more than a trace of invert sugar, and that further investigation is unnecessary.

D.—BEETROOT SEEDS.

For the control of the sale of beetroot seeds the following regulations, known as the "Magdeburg Rules," have been adopted in Germany.³ Although they are not in any way accepted in this country they are of value as a standard of reference, and include the following:—

The beetroot seed must be delivered in a sound and healthy condition, and must satisfy the following requirements.

1. 1 kg. of beetroot seeds shall produce at least 70,000 buds in fourteen days.

2. Of these, at least 46,000 must have sprouted in six days.

3. Of 100 seed nodules at least 75 must have germinated.

4. An aqueous content of up to 15 per cent. inclusive is normal; up to 17 per cent. inclusive, the goods are still saleable; in cases where the aqueous content exceeds 15-17 per cent., a percentage corresponding to the weight of water is to be made good.

5. Foreign ingredients are permissible up to 3 per cent. inclusive; up to 5 per cent. inclusive of foreign matter, the goods are still saleable; in cases where the foreign ingredients exceed 3-5 per cent., a percentage corresponding to the weight of foreign matter is to be made good.

6. An infraction of any of the above rules renders the goods unsaleable.

7. Differences in the analyses are finally settled by taking the mean between a fresh analysis performed at that station at which the

¹ For a method proposed by Urban, who uses the juice obtained by cold digestion and a copper solution free from alkali, see *Z. Zuckerind. Böhm.*, 1910, 34, 288.

² *Deutsche Zuckerindustrie*, 1909, 34, 973.

³ *Z. Ver. deut. Zuckerind.*, 1896, 46, 531.

analysis in dispute was made and an analysis made in the laboratory of the Verein für Zuckerindustrie, Berlin, or in the Experimental Station, Bernburg.

The regulations obtaining in other countries differ in various points from those cited above,¹ and in Germany itself a few of these rules are considered to stand in need of revision.

II. BEETROOT JUICE, THIN JUICE, AND THE PRODUCTS OCCURRING IN THE WORKING UP OF THE JUICE.

WASTE WATER, EXTRACTED SLICES, PRESSED MUD.

I. BEETROOT JUICE, THIN JUICE.

Although, in the case of beetroot juice, it has long been regarded as an invariable rule that the juice should be analysed immediately after it has been prepared, it is considered that samples of juice, and especially of diffusion juice, may be kept without decomposition for a longer time, by the addition of small quantities of chloroform, formaldehyde, carbon bisulphide and similar substances, and especially by the addition of mercuric chloride, so that trustworthy average samples corresponding to a longer period of working may be obtained. Pellet² has shown that the very small quantities of mercuric chloride (sublimate pastilles³) recommended, amongst others, by Courtonne,⁴ may not be sufficient, and advises the addition of such a quantity of mercuric chloride that a detectable amount remains undecomposed; its poisonous nature, however, renders the handling of a concentrated solution by no means an easy matter, and moreover, Pellet has shown that 1 g. per litre of this salt raises the hydrometric reading by about 2°·15 Brix; and finally, in cases where the invert sugar-content is to be estimated, the removal of a second parallel sample, free from mercuric chloride, is necessary. Further, Claassen⁵ and Herrmann⁶ have shown, by a series of careful experiments, that not only the usual maximum amount of mercuric chloride (0·05 per cent.), but also that of chloroform (0·5-1 per cent.), of formaldehyde (0·1-0·35 per cent.), and of similar agents, do not suffice under all conditions to ensure the necessary perfect preservation of the diffusion juice (extraction juice, expressed juice), even for a short time (about two hours). If, again, the addition of basic lead acetate solution which

¹ For the so-called "New Vienna Rules," see *Jahr. und Adressenbuch der Zuckerfabriken Österreich-Ungarns*, 1909-10, p. 410.

² *Bull. Assoc. Chim. Sucr.*, 1901, 19, 725.

³ *Zentralbl. Zuckerind.*, 1896, p. 953.

⁵ *Zentralbl. Zuckerind.*, 1902, 11, 10 and 100.

⁴ *Deutsche Zuckerindustrie*, 1899, p. 1206.

⁶ *Ibid.*, 1904, 12, 489 and 701.

was the usual practice at one time is not desired, since its volume must amount to 10 or at least 5 per cent. of the total volume and the change in volume caused thereby must be taken into account, the individual samples must be analysed in order to obtain correct results. These samples are taken (*e.g.* from the outlet pipes of the measuring back) at convenient, short intervals, in which operations outlet cocks, valves, pipes, etc., must be kept thoroughly clean. The samples must be collected in clean vessels provided with stoppers, and the determinations of density and rotatory power should be made immediately if possible, and in any case within one to one and a half hours. The collection of an average sample (which is best withdrawn continuously) for the purpose of comparison with, and control of the density determinations only, is permissible and to be recommended, since in respect of this determination no appreciable variation occurs within four to six hours. Juice, sterilised in the so-called Weck's vessels, remains unchanged indefinitely.

A.—DETERMINATION OF SPECIFIC GRAVITY.

The specific gravity may be determined with the requisite speed and accuracy by means of the hydrometer, the pycnometer, or Mohr's hydrostatic balance.

The solution must first be freed from air; this may be effected by leaving it to stand for some time, or by placing it in a flask and exhausting the latter. Brumme¹ has constructed an apparatus for removing air, and Wohryzek² has devised a very handy cylinder (burette-cylinder) for the immersion of the hydrometer, etc.

The hydrometers generally used in the operations of sugar manufacture are the saccharometer of Balling, graduated by immersion of the instrument in solutions of pure sugar of known concentration and that of Brix, graduated in the same way. The slight differences between these scales are of no importance in practical work. In the case of pure sugar solutions, these hydrometers give the percentage weight of sugar corresponding to the specific gravity directly. With crude manufacturing products, on the contrary, the "degrees Brix" are not equivalent to the amount of pure sugar present, but represent the total dry substance, *i.e.*, not only sugar, but soluble substances other than sugar. Since, however, the latter influence the specific gravity of the solution to a degree different from that of the sugar, in such cases the saccharometer does not give the true content of all dissolved substances, *i.e.* the "actual" dry substance, but only the so-called "apparent" dry substance, the difference between which and

¹ *Oesterr. Chem. Zeit.*, 1898, p. 314.

² *Oesterr.-Ungar. Zeitschr.*, 1910, 39, 56.

the true value is the greater the larger the content of substances other than sugar.

With regard to the relation between the sugar-content and the specific gravity of aqueous solutions, the investigations of Plato, Domke, and Harting, published in detail in the "Wissenschaftliche Abhandlungen der k. Normal-Eichungs-Kommission" (Berlin, 1900), are by far the most exact and trustworthy. Two Tables,¹ which are based on 134 experiments carried out between 14° and 26°, and calculated for a temperature=15°, give the true specific gravities of sugar solutions from 0.1-70.9 per cent. and to 100 per cent. of sugar respectively. In the first Table the specific gravities are calculated to 15° referred to water at 15°; in the second to 20° referred to water at 4°. The second Table² should, according to international rules, be used exclusively for all determinations, since the normal temperature of 20° is agreed upon for all operations of sugar analysis; actually, however, even in Germany, this temperature is very little used in practice, partly owing to reluctance to discontinue the use of vessels graduated at 17°.5 and the corresponding Tables (ostensibly on account of the comparison of results), and partly because the latter indicate the relation between specific gravity and degrees Baumé in a way suitable for many purposes. For many commercial products such as syrups, molasses, concentrated desaccharification liquors, and similar materials, the results are still always required in degrees Baumé, although the Baumé scale is quite empirical and the degrees stand in no definite relation to the sugar-content of the solution. Moreover, there exists both the "old" and the "new" degrees Baumé; the latter, although the more accurately calculated, are less used than the "old" degrees for commercial purposes.

Taking into consideration the prevailing conditions and actual requirements, it is not necessary to give Plato's Tables. The following Table compiled by Matejczek³ and Scheibler,⁴ although less exact, is that generally used at the present time.

¹ *Z. Ver. deut. Zuckerind.*, 1900, 50, 982, 1005, 1107, and 1123.

² See Lippmann, *Chemie der Zuckerarten*, pp. 1071 *et seq.*

³ *Z. Ver. deut. Zuckerind.*, 1865, 15, 580; 1874, 24, 827.

⁴ *Ibid.*, 1870, 20, 263; 1874, 24, 950; 1877, 27, 32.

[TABLE 46 follows.]

Table 46.¹

For comparison between the Percentage Weight or Degrees according to Brix, Specific Gravity, and Degrees according to Baumé, for pure Sugar Solutions from 0 to 95 per cent.; Temperature: 17°.5. (Scheibler and Matejczek.)

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
0.0	1.00000	0.0	0.0	4.1	1.01610	2.3	2.3	8.2	1.03270	4.6	4.6
0.1	1.00038	0.1	0.1	4.2	1.01650	2.4	2.3	8.3	1.03311	4.7	4.6
0.2	1.00077	0.1	0.1	4.3	1.01690	2.4	2.4	8.4	1.03352	4.8	4.7
0.3	1.00116	0.2	0.2	4.4	1.01730	2.5	2.4	8.5	1.03393	4.8	4.7
0.4	1.00155	0.2	0.2	4.5	1.01770	2.55	2.5	8.6	1.03434	4.9	4.8
0.5	1.00193	0.3	0.3	4.6	1.01810	2.6	2.6	8.7	1.03475	4.9	4.8
0.6	1.00232	0.3	0.3	4.7	1.01850	2.7	2.6	8.8	1.03517	5.0	4.9
0.7	1.00271	0.4	0.4	4.8	1.01890	2.7	2.7	8.9	1.03558	5.0	4.9
0.8	1.00310	0.45	0.4	4.9	1.01930	2.8	2.7	9.0	1.03599	5.1	5.0
0.9	1.00349	0.5	0.5	5.0	1.01970	2.8	2.8	9.1	1.03640	5.2	5.0
1.0	1.00388	0.6	0.55	5.1	1.02010	2.9	2.8	9.2	1.03682	5.2	5.1
1.1	1.00427	0.6	0.6	5.2	1.02051	2.95	2.9	9.3	1.03723	5.3	5.2
1.2	1.00466	0.7	0.7	5.3	1.02091	3.0	2.9	9.4	1.03765	5.3	5.2
1.3	1.00505	0.7	0.7	5.4	1.02131	3.1	3.0	9.5	1.03806	5.4	5.3
1.4	1.00544	0.8	0.8	5.5	1.02171	3.1	3.0	9.6	1.03848	5.4	5.3
1.5	1.00583	0.85	0.8	5.6	1.02211	3.2	3.1	9.7	1.03889	5.5	5.4
1.6	1.00622	0.9	0.9	5.7	1.02252	3.2	3.2	9.8	1.03931	5.55	5.4
1.7	1.00662	1.0	0.9	5.8	1.02292	3.3	3.2	9.9	1.03972	5.6	5.5
1.8	1.00701	1.0	1.0	5.9	1.02333	3.35	3.3	10.0	1.04014	5.7	5.5
1.9	1.00740	1.1	1.05	6.0	1.02373	3.4	3.3	10.1	1.04055	5.7	5.6
2.0	1.00779	1.1	1.1	6.1	1.02413	3.5	3.4	10.2	1.04097	5.8	5.7
2.1	1.00818	1.2	1.2	6.2	1.02454	3.5	3.4	10.3	1.04139	5.8	5.7
2.2	1.00858	1.2	1.2	6.3	1.02494	3.6	3.5	10.4	1.04180	5.9	5.8
2.3	1.00897	1.3	1.3	6.4	1.02535	3.6	3.6	10.5	1.04222	5.9	5.8
2.4	1.00936	1.4	1.3	6.5	1.02575	3.7	3.6	10.6	1.04264	6.0	5.9
2.5	1.00976	1.4	1.4	6.6	1.02616	3.7	3.7	10.7	1.04306	6.1	5.9
2.6	1.01015	1.5	1.4	6.7	1.02657	3.8	3.7	10.8	1.04348	6.1	6.05
2.7	1.01055	1.5	1.5	6.8	1.02697	3.9	3.8	10.9	1.04390	6.2	6.5
2.8	1.01094	1.6	1.55	6.9	1.02738	3.9	3.8	11.0	1.04431	6.2	6.1
2.9	1.01134	1.6	1.6	7.0	1.02779	4.0	3.9	11.1	1.04473	6.3	6.2
3.0	1.01173	1.7	1.7	7.1	1.02819	4.0	3.9	11.2	1.04515	6.3	6.2
3.1	1.01213	1.8	1.7	7.2	1.02860	4.1	4.0	11.3	1.04557	6.4	6.3
3.2	1.01252	1.8	1.8	7.3	1.02901	4.1	4.1	11.4	1.04599	6.5	6.3
3.3	1.01292	1.9	1.8	7.4	1.02942	4.2	4.1	11.5	1.04641	6.5	6.4
3.4	1.01332	1.9	1.9	7.5	1.02983	4.25	4.2	11.6	1.04683	6.6	6.4
3.5	1.01371	2.0	1.9	7.6	1.03024	4.3	4.2	11.7	1.04726	6.6	6.5
3.6	1.01411	2.0	2.0	7.7	1.03064	4.4	4.3	11.8	1.04768	6.7	6.55
3.7	1.01451	2.1	2.0	7.8	1.03105	4.4	4.3	11.9	1.04810	6.7	6.6
3.8	1.01491	2.2	2.1	7.9	1.03146	4.5	4.4	12.0	1.04852	6.8	6.7
3.9	1.01531	2.2	2.2	8.0	1.03187	4.5	4.4	12.1	1.04894	6.8	6.7
4.0	1.01570	2.3	2.2	8.1	1.03228	4.6	4.5	12.2	1.04937	6.9	6.8

¹ For more recent Tables based on that drawn up by the International Commission for Standard Methods of Sugar Analysis, see J. Domke, *Z. Ver. deut. Zuckerind.*, 1912, 52, 302-311; also, *J. Soc. Chem. Ind.*, 1912, 31, 449.

Table 46—continued.

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
12.3	1.04979	7.0	6.8	17.9	1.07397	10.1	9.9	23.5	1.09915	13.2	13.0
12.4	1.05021	7.0	6.9	18.0	1.07441	10.1	10.0	23.6	1.09961	13.3	13.0
12.5	1.05064	7.1	6.9	18.1	1.07485	10.2	10.0	23.7	1.10007	13.3	13.1
12.6	1.05106	7.1	7.0	18.2	1.07530	10.3	10.1	23.8	1.10053	13.4	13.15
12.7	1.05149	7.2	7.05	18.3	1.07574	10.3	10.1	23.9	1.10099	13.5	13.2
12.8	1.05191	7.2	7.1	18.4	1.07618	10.4	10.2	24.0	1.10145	13.5	13.3
12.9	1.05233	7.3	7.2	18.5	1.07662	10.4	10.2	24.1	1.10191	13.6	13.3
13.0	1.05276	7.4	7.2	18.6	1.07706	10.5	10.3	24.2	1.10237	13.6	13.4
13.1	1.05318	7.4	7.3	18.7	1.07751	10.5	10.35	24.3	1.10283	13.7	13.4
13.2	1.05361	7.5	7.3	18.8	1.07795	10.6	10.4	24.4	1.10329	13.7	13.5
13.3	1.05404	7.5	7.4	18.9	1.07839	10.6	10.5	24.5	1.10375	13.8	13.5
13.4	1.05446	7.6	7.4	19.0	1.07884	10.7	10.5	24.6	1.10421	13.8	13.6
13.5	1.05489	7.6	7.5	19.1	1.07928	10.8	10.6	24.7	1.10468	13.9	13.6
13.6	1.05532	7.7	7.5	19.2	1.07973	10.8	10.6	24.8	1.10514	14.0	13.7
13.7	1.05574	7.75	7.6	19.3	1.08017	10.9	10.7	24.9	1.10560	14.0	13.75
13.8	1.05617	7.8	7.65	19.4	1.08062	10.9	10.7	25.0	1.10607	14.1	13.8
13.9	1.05660	7.9	7.7	19.5	1.08106	11.0	10.8	25.1	1.10653	14.1	13.9
14.0	1.05703	7.9	7.8	19.6	1.08151	11.1	10.85	25.2	1.10700	14.2	13.9
14.1	1.05746	8.0	7.8	19.7	1.08196	11.1	10.9	25.3	1.10746	14.2	14.0
14.2	1.05789	8.0	7.9	19.8	1.08240	11.2	11.0	25.4	1.10793	14.3	14.0
14.3	1.05831	8.1	7.9	19.9	1.08285	11.2	11.0	25.5	1.10839	14.3	14.1
14.4	1.05874	8.1	8.0	20.0	1.08329	11.3	11.1	25.6	1.10886	14.4	14.1
14.5	1.05917	8.2	8.0	20.1	1.08374	11.3	11.1	25.7	1.10932	14.5	14.2
14.6	1.05960	8.3	8.1	20.2	1.08419	11.4	11.2	25.8	1.10979	14.5	14.2
14.7	1.06003	8.3	8.15	20.3	1.08464	11.5	11.2	25.9	1.11026	14.6	14.3
14.8	1.06047	8.4	8.2	20.4	1.08509	11.5	11.3	26.0	1.11072	14.6	14.35
14.9	1.06090	8.4	8.3	20.5	1.08553	11.6	11.3	26.1	1.11119	14.7	14.4
15.0	1.06133	8.5	8.3	20.6	1.08599	11.6	11.4	26.2	1.11166	14.7	14.5
15.1	1.06176	8.5	8.4	20.7	1.08643	11.7	11.45	26.3	1.11213	14.8	14.5
15.2	1.06219	8.55	8.4	20.8	1.08688	11.7	11.5	26.4	1.11259	14.85	14.6
15.3	1.06262	8.6	8.5	20.9	1.08733	11.8	11.6	26.5	1.11306	14.9	14.6
15.4	1.06306	8.7	8.5	21.0	1.08778	11.8	11.6	26.6	1.11353	15.0	14.7
15.5	1.06349	8.8	8.6	21.1	1.08824	11.9	11.7	26.7	1.11400	15.0	14.7
15.6	1.06392	8.8	8.65	21.2	1.08869	11.95	11.7	26.8	1.11447	15.1	14.8
15.7	1.06436	8.9	8.7	21.3	1.08914	12.0	11.8	26.9	1.11494	15.1	14.8
15.8	1.06479	8.9	8.8	21.4	1.08959	12.0	11.8	27.0	1.11541	15.2	14.9
15.9	1.06522	9.0	8.8	21.5	1.09004	12.1	11.9	27.1	1.11588	15.2	14.9
16.0	1.06566	9.0	8.9	21.6	1.09049	12.1	11.95	27.2	1.11635	15.3	15.0
16.1	1.06609	9.1	8.9	21.7	1.09095	12.2	12.0	27.3	1.11682	15.3	15.1
16.2	1.06653	9.2	9.0	21.8	1.09140	12.3	12.05	27.4	1.11729	15.4	15.1
16.3	1.06696	9.2	9.0	21.9	1.09185	12.3	12.1	27.5	1.11776	15.5	15.2
16.4	1.06740	9.3	9.1	22.0	1.09231	12.4	12.2	27.6	1.11824	15.5	15.2
16.5	1.06783	9.3	9.1	22.1	1.09276	12.5	12.2	27.7	1.11871	15.6	15.3
16.6	1.06827	9.4	9.2	22.2	1.09321	12.5	12.3	27.8	1.11918	15.6	15.3
16.7	1.06871	9.4	9.25	22.3	1.09367	12.6	12.3	27.9	1.11965	15.7	15.4
16.8	1.06914	9.5	9.3	22.4	1.09412	12.6	12.4	28.0	1.12013	15.7	15.4
16.9	1.06958	9.5	9.4	22.5	1.09458	12.7	12.4	28.1	1.12060	15.8	15.5
17.0	1.07002	9.6	9.4	22.6	1.09503	12.7	12.5	28.2	1.12107	15.8	15.55
17.1	1.07046	9.7	9.5	22.7	1.09549	12.8	12.55	28.3	1.12155	15.8	15.6
17.2	1.07090	9.75	9.5	22.8	1.09595	12.85	12.6	28.4	1.12202	16.0	15.7
17.3	1.07133	9.8	9.6	22.9	1.09640	12.9	12.7	28.5	1.12250	16.0	15.7
17.4	1.07177	9.8	9.6	23.0	1.09686	13.0	12.7	28.6	1.12297	16.1	15.8
17.5	1.07221	9.9	9.7	23.1	1.09732	13.0	12.8	28.7	1.12345	16.1	15.9
17.6	0.07265	9.9	9.7	23.2	1.09777	13.1	12.8	28.8	1.12393	16.2	15.9
17.7	1.07309	10.0	9.8	23.3	1.09823	13.1	12.9	28.9	1.12440	16.2	15.9
17.8	1.07353	10.0	9.9	23.4	1.09869	13.2	12.9	29.0	1.12488	16.3	16.0

Table 46—continued.

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
29·1	1·12536	16·3	16 0	34·7	1·15262	19·4	19·1	40·3	1·18098	22·5	22·1
29·2	1·12583	16·4	16·1	34·8	1·15312	19·5	19·1	40·4	1·18150	22·5	22·1
29·3	1·12631	16·5	16·1	34·9	1·15362	19·5	19·2	40·5	1·18201	22·6	22·2
29·4	1·12679	16·5	16·2	35·0	1·15411	19·6	19·2	40·6	1·18253	22·6	22·2
29·5	1·12727	16·6	16·25	35·1	1·15461	19·65	19·3	40·7	1·18305	22·7	22·3
29·6	1·12775	16·6	16·3	35·2	1·15511	19·7	19·3	40·8	1·18357	22·8	22·3
29·7	1·12823	16·7	16·4	35·3	1·15561	19·8	19·4	40·9	1·18408	22·8	22·4
29·8	1·12871	16·7	16·4	35·4	1·15611	19·8	19·4	41·0	1·18460	22·9	22·4
29·9	1·12919	16·8	16·5	35·5	1·15661	19·9	19·5	41·1	1·18512	22·9	22·5
30·0	1·12967	16·8	16·5	35·6	1·15710	19·9	19·55	41·2	1·18564	23·0	22·5
30·1	1·13015	16·9	16·6	35·7	1·15760	20·0	19·6	41·3	1·18616	23·0	22·6
30·2	1·13063	16·95	16·6	35·8	1·15810	20·0	19·65	41·4	1·18668	23·1	22·65
30·3	1·13111	17·0	16·7	35·9	1·15861	20·1	19·7	41·5	1·18720	23·1	22·7
30·4	1·13159	17·1	16·7	36·0	1·15911	20·1	19·8	41·6	1·18772	23·2	22·75
30·5	1·13207	17·1	16·8	36·1	1·15961	20·2	19·8	41·7	1·18824	23·25	22·8
30·6	1·13255	17·2	16·85	36·2	1·16011	20·25	19·9	41·8	1·18877	23·3	22·9
30·7	1·13304	17·2	16·9	36·3	1·16061	20·3	19·9	41·9	1·18929	23·4	22·9
30·8	1·13352	17·3	17·0	36·4	1·16111	20·4	20·0	42·0	1·18981	23·4	23·0
30·9	1·13400	17·3	17·0	36·5	1·16162	20·4	20·0	42·1	1·19033	23·5	23·0
31·0	1·13449	17·4	17·1	36·6	1·16212	20·5	20·1	42·2	1·19086	23·5	23·1
31·1	1·13497	17·45	17·1	36·7	1·16262	20·5	20·1	42·3	1·19138	23·6	23·1
31·2	1·13545	17·5	17·2	36·8	1·16313	20·6	20·2	42·4	1·19190	23·6	23·2
31·3	1·13594	17·6	17·2	36·9	1·16363	20·6	20·2	42·5	1·19243	23·7	23·2
31·4	1·13642	17·6	17·3	37·0	1·16413	20·7	20·3	42·6	1·19295	23·7	23·3
31·5	1·13691	17·7	17·3	37·1	1·16464	20·7	20·35	42·7	1·19348	23·8	23·3
31·6	1·13740	17·7	17·4	37·2	1·16514	20·8	20·4	42·8	1·19400	23·8	23·4
31·7	1·13788	17·8	17·4	37·3	1·16565	20·9	20·5	42·9	1·19453	23·9	23·45
31·8	1·13837	17·8	17·5	37·4	1·16616	20·9	20·5	43·0	1·19505	23·95	23·5
31·9	1·13885	17·9	17·55	37·5	1·16666	21·0	20·6	43·1	1·19558	24·0	23·55
32·0	1·13934	17·95	17·6	37·6	1·16717	21·0	20·6	43·2	1·19611	24·1	23·6
32·1	1·13983	18·0	17·7	37·7	1·16768	21·1	20·7	43·3	1·19663	24·1	23·7
32·2	1·14032	18·0	17·7	37·8	1·16818	21·1	20·7	43·4	1·19716	24·2	23·7
32·3	1·14081	18·1	17·8	37·9	1·16869	21·2	20·8	43·5	1·19769	24·2	23·8
32·4	1·14129	18·2	17·8	38·0	1·16920	21·2	20·8	43·6	1·19822	24·3	23·8
32·5	1·14178	18·2	17·9	38·1	1·16971	21·3	20·9	43·7	1·19875	24·3	23·9
32·6	1·14227	18·3	17·9	38·2	1·17022	21·35	20·9	43·8	1·19927	24·4	23·9
32·7	1·14276	18·3	18·0	38·3	1·17072	21·4	21·0	43·9	1·19980	24·4	24·0
32·8	1·14325	18·4	18·0	38·4	1·17123	21·5	21·05	44·0	1·20033	24·5	24·0
32·9	1·14374	18·4	18·1	38·5	1·17174	21·5	21·1	44·1	1·20086	24·55	24·1
33·0	1·14423	18·5	18·15	38·6	1·17225	21·6	21·15	44·2	1·20139	24·6	24·1
33·1	1·14472	18·55	18·2	38·7	1·17276	21·6	21·2	44·3	1·20192	24·65	24·2
33·2	1·14521	18·6	18·25	38·8	1·17327	21·7	21·3	44·4	1·20245	24·7	24·2
33·3	1·14570	18·7	18·3	38·9	1·17379	21·7	21·3	44·5	1·20299	24·8	24·3
33·4	1·14620	18·7	18·4	39·0	1·17430	21·8	21·4	44·6	1·20352	24·8	24·35
33·5	1·14669	18·8	18·4	39·1	1·17481	21·8	21·4	44·7	1·20405	24·9	24·4
33·6	1·14718	18·8	18·5	39·2	1·17532	21·9	21·5	44·8	1·20458	24·9	24·45
33·7	1·14767	18·9	18·5	39·3	1·17583	21·9	21·5	44·9	1·20512	25·0	24·5
33·8	1·14817	18·9	18·6	39·4	1·17635	22·0	21·6	45·0	1·20565	25·0	24·6
33·9	1·14866	19·0	18·6	39·5	1·17686	22·05	21·6	45·1	1·20618	25·1	24·6
34·0	1·14915	19·05	18·7	39·6	1·17737	22·1	21·7	45·2	1·20672	25·1	24·7
34·1	1·14965	19·1	18·7	39·7	1·17789	22·2	21·7	45·3	1·20725	25·2	24·7
34·2	1·15014	19·2	18·8	39·8	1·17840	22·2	21·8	45·4	1·20779	25·2	24·8
34·3	1·15064	19·2	18·85	39·9	1·17892	22·3	21·85	45·5	1·20832	25·3	24·8
34·4	1·15113	19·3	18·9	40·0	1·17943	22·3	21·9	45·6	1·20886	25·4	24·9
34·5	1·15163	19·3	18·95	40·1	1·17995	22·4	22·0	45·7	1·20939	25·4	24·9
34·6	1·15213	19·4	19·0	40·2	1·18046	22·4	22·0	45·8	1·20993	25·5	25·0

Table 46—continued.

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
45.9	1.21046	25.5	25.0	51.5	1.24111	28.5	28.0	57.1	1.27293	31.5	30.9
46.0	1.21100	25.6	25.1	51.6	1.24166	28.6	28.0	57.2	1.27351	31.5	30.9
46.1	1.21154	25.6	25.1	51.7	1.24222	28.6	28.1	57.3	1.27409	31.6	31.0
46.2	1.21208	25.7	25.2	51.8	1.24278	28.7	28.1	57.4	1.27464	31.6	31.0
46.3	1.21261	25.7	25.2	51.9	1.24334	28.7	28.2	57.5	1.27525	31.7	31.1
46.4	1.21315	25.8	25.3	52.0	1.24390	28.8	28.2	57.6	1.27583	31.7	31.1
46.5	1.21369	25.8	25.35	52.1	1.24446	28.8	28.3	57.7	1.27641	31.8	31.2
46.6	1.21423	25.9	25.4	52.2	1.24502	28.9	28.3	57.8	1.27699	31.8	31.2
46.7	1.21477	25.95	25.45	52.3	1.24558	28.9	28.4	57.9	1.27758	31.9	31.3
46.8	1.21531	26.0	25.5	52.4	1.24614	29.0	28.4	58.0	1.27816	31.9	31.3
46.9	1.21585	26.1	25.6	52.5	1.24670	29.0	28.5	58.1	1.27874	32.0	31.4
47.0	1.21639	26.1	25.6	52.6	1.24726	29.1	28.5	58.2	1.27932	32.0	31.4
47.1	1.21693	26.2	25.7	52.7	1.24782	29.15	28.6	58.3	1.27991	32.1	31.5
47.2	1.21747	26.2	25.7	52.8	1.24839	29.2	28.65	58.4	1.28049	32.15	31.5
47.3	1.21802	26.3	25.8	52.9	1.24895	29.2	28.7	58.5	1.28107	32.2	31.6
47.4	1.21856	26.3	25.8	53.0	1.24951	29.3	28.75	58.6	1.28166	32.3	31.6
47.5	1.21910	26.4	25.9	53.1	1.25008	29.4	28.8	58.7	1.28224	32.3	31.7
47.6	1.21964	26.4	25.9	53.2	1.25064	29.4	28.85	58.8	1.28283	32.4	31.7
47.7	1.22019	26.5	26.0	53.3	1.25120	29.5	28.9	58.9	1.28342	32.4	31.8
47.8	1.22073	26.5	26.0	53.4	1.25177	29.5	28.9	59.0	1.28400	32.5	31.85
47.9	1.22127	26.6	26.1	53.5	1.25233	29.6	29.0	59.1	1.28459	32.5	31.9
48.0	1.22182	26.6	26.1	53.6	1.25290	29.6	29.1	59.2	1.28518	32.6	31.95
48.1	1.22236	26.7	26.2	53.7	1.25347	29.7	29.1	59.3	1.28576	32.6	32.0
48.2	1.22291	26.75	26.2	53.8	1.25403	29.7	29.2	59.4	1.28635	32.7	32.05
48.3	1.22345	26.8	26.3	53.9	1.25460	29.8	29.2	59.5	1.28694	32.7	32.1
48.4	1.22400	26.9	26.35	54.0	1.25517	29.8	29.3	59.6	1.28753	32.8	32.15
48.5	1.22455	26.9	26.4	54.1	1.25573	29.9	29.3	59.7	1.28812	32.8	32.2
48.6	1.22509	27.0	26.45	54.2	1.25630	29.9	29.4	59.8	1.28871	32.9	32.3
48.7	1.22564	27.0	26.5	54.3	1.25687	30.0	29.4	59.9	1.28930	32.9	32.3
48.8	1.22619	27.1	26.6	54.4	1.25744	30.05	29.5	60.0	1.28989	33.0	32.4
48.9	1.22673	27.1	26.6	54.5	1.25801	30.1	29.5	60.1	1.29048	33.0	32.4
49.0	1.22728	27.2	26.7	54.6	1.25857	30.2	29.6	60.2	1.29107	33.1	32.5
49.1	1.22783	27.2	26.7	54.7	1.25914	30.2	29.6	60.3	1.29166	33.1	32.5
49.2	1.22838	27.3	26.8	54.8	1.25971	30.3	29.7	60.4	1.29225	33.2	32.6
49.3	1.22893	27.3	26.8	54.9	1.26028	30.3	29.7	60.5	1.29284	33.2	32.6
49.4	1.22948	27.4	26.9	55.0	1.26086	30.4	29.8	60.6	1.29343	33.3	32.7
49.5	1.23003	27.4	26.9	55.1	1.26143	30.4	29.8	60.7	1.29403	33.35	32.7
49.6	1.23058	27.5	27.0	55.2	1.26200	30.5	29.9	60.8	1.29462	33.4	32.8
49.7	1.23113	27.6	27.0	55.3	1.26257	30.5	29.9	60.9	1.29521	33.45	32.8
49.8	1.23168	27.6	27.1	55.4	1.26314	30.6	30.0	61.0	1.29581	33.5	32.9
49.9	1.23223	27.7	27.1	55.5	1.26372	30.6	30.05	61.1	1.29640	33.6	32.9
50.0	1.23278	27.7	27.2	55.6	1.26429	30.7	30.1	61.2	1.29700	33.6	33.0
50.1	1.23334	27.8	27.2	55.7	1.26486	30.7	30.15	61.3	1.29759	33.7	33.0
50.2	1.23389	27.8	27.3	55.8	1.26544	30.8	30.2	61.4	1.29819	33.7	33.1
50.3	1.23444	27.9	27.3	55.9	1.26601	30.8	30.25	61.5	1.29878	33.8	33.1
50.4	1.23499	27.9	27.4	56.0	1.26658	30.9	30.3	61.6	1.29938	33.8	33.2
50.5	1.23555	28.0	27.45	56.1	1.26716	30.9	30.4	61.7	1.29998	33.9	33.2
50.6	1.23610	28.0	27.5	56.2	1.26773	31.0	30.4	61.8	1.30057	33.9	33.3
50.7	1.23666	28.1	27.55	56.3	1.26831	31.05	30.5	61.9	1.30117	34.0	33.3
50.8	1.23721	28.1	27.6	56.4	1.26889	31.1	30.5	62.0	1.30177	34.0	33.4
50.9	1.23777	28.2	27.7	56.5	1.26946	31.2	30.6	62.1	1.30237	34.1	33.4
51.0	1.23832	28.2	27.7	56.6	1.27004	31.2	30.6	62.2	1.30297	34.1	33.5
51.1	1.23888	28.3	27.8	56.7	1.27062	31.3	30.7	62.3	1.30356	34.2	33.5
51.2	1.23943	28.35	27.8	56.8	1.27120	31.3	30.7	62.4	1.30416	34.2	33.6
51.3	1.23999	28.4	27.9	56.9	1.27177	31.4	30.8	62.5	1.30476	34.3	33.6
51.4	1.24055	28.5	27.9	57.0	1.27235	31.4	30.8	62.6	1.30536	34.3	33.7

Table 46—continued.

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
62·7	1·30596	34·4	33·7	68·3	1·34053	37·3	36·6	73·9	1·37575	40·1	39·3
62·8	1·30657	34·4	33·8	68·4	1·34085	37·3	36·6	74·0	1·37639	40·1	39·4
62·9	1·30717	34·5	33·8	68·5	1·34148	37·4	36·7	74·1	1·37704	40·2	39·4
63·0	1·30777	34·5	33·9	68·6	1·34210	37·4	36·7	74·2	1·37768	40·2	39·5
63·1	1·30837	34·6	33·9	68·7	1·34273	37·5	36·8	74·3	1·37833	40·3	39·5
63·2	1·30897	34·6	34·0	68·8	1·34335	37·5	36·8	74·4	1·37898	40·3	39·6
63·3	1·30958	34·7	34·0	68·9	1·34398	37·6	36·9	74·5	1·37962	40·4	39·6
63·4	1·31018	34·7	34·1	69·0	1·34460	37·6	36·9	74·6	1·38027	40·4	39·7
63·5	1·31078	34·8	34·1	69·1	1·34523	37·7	37·0	74·7	1·38092	40·5	39·7
63·6	1·31139	34·85	34·2	69·2	1·34585	37·7	37·0	74·8	1·38157	40·5	39·8
63·7	1·31199	34·9	34·2	69·3	1·34648	37·8	37·1	74·9	1·38222	40·6	39·8
63·8	1·31260	34·95	34·3	69·4	1·34711	37·8	37·1	75·0	1·38287	40·6	39·9
63·9	1·31320	35·0	34·3	69·5	1·34774	37·9	37·2	75·1	1·38352	40·7	39·9
64·0	1·31381	35·1	34·4	69·6	1·34836	37·9	37·2	75·2	1·38417	40·7	40·0
64·1	1·31442	35·1	34·4	69·7	1·34899	38·0	37·3	75·3	1·38482	40·8	40·0
64·2	1·31502	35·2	34·5	69·8	1·34962	38·0	37·3	75·4	1·38547	40·8	40·1
64·3	1·31563	35·2	34·5	69·9	1·35025	38·1	37·4	75·5	1·38612	40·9	40·1
64·4	1·31624	35·3	34·6	70·0	1·35088	38·1	37·4	75·6	1·38677	40·9	40·2
64·5	1·31684	35·3	34·6	70·1	1·35151	38·2	37·5	75·7	1·38743	41·0	40·2
64·6	1·31745	35·4	34·7	70·2	1·35214	38·2	37·5	75·8	1·38808	41·0	40·3
64·7	1·31806	35·4	34·7	70·3	1·35277	38·3	37·6	75·9	1·38873	41·1	40·3
64·8	1·31867	35·5	34·8	70·4	1·35340	38·3	37·6	76·0	1·38939	41·1	40·4
64·9	1·31928	35·5	34·8	70·5	1·35403	38·4	37·7	76·1	1·39004	41·2	40·4
65·0	1·31989	35·6	34·9	70·6	1·35466	38·4	37·7	76·2	1·39070	41·2	40·5
65·1	1·32050	35·6	34·95	70·7	1·35530	38·5	37·8	76·3	1·39135	41·3	40·5
65·2	1·32111	35·7	35·0	70·8	1·35593	38·5	37·8	76·4	1·39201	41·3	40·6
65·3	1·32172	35·7	35·05	70·9	1·35656	38·6	37·9	76·5	1·39266	41·4	40·6
65·4	1·32233	35·8	35·1	71·0	1·35720	38·6	37·9	76·6	1·39332	41·4	40·7
65·5	1·32294	35·8	35·15	71·1	1·35783	38·7	37·9	76·7	1·39397	41·5	40·7
65·6	1·32355	35·9	35·2	71·2	1·35847	38·7	38·0	76·8	1·39463	41·5	40·8
65·7	1·32417	35·9	35·25	71·3	1·35910	38·8	38·0	76·9	1·39529	41·6	40·8
65·8	1·32478	36·0	35·3	71·4	1·35974	38·8	38·1	77·0	1·39595	41·6	40·8
65·9	1·32539	36·0	35·35	71·5	1·36037	38·9	38·1	77·1	1·39660	41·7	40·9
66·0	1·32601	36·1	35·4	71·6	1·36101	38·9	38·2	77·2	1·39726	41·7	40·9
66·1	1·32662	36·1	35·5	71·7	1·36164	39·0	38·2	77·3	1·39792	41·8	41·0
66·2	1·32724	36·2	35·5	71·8	1·36228	39·0	38·3	77·4	1·39858	41·8	41·0
66·3	1·32785	36·2	35·6	71·9	1·36292	39·1	38·3	77·5	1·39924	41·9	41·1
66·4	1·32847	36·3	35·6	72·0	1·36355	39·1	38·4	77·6	1·39990	41·9	41·1
66·5	1·32908	36·3	35·7	72·1	1·36419	39·2	38·4	77·7	1·40056	42·0	41·2
66·6	1·32970	36·4	35·7	72·2	1·36483	39·2	38·5	77·8	1·40122	42·0	41·2
66·7	1·33031	36·4	35·8	72·3	1·36547	39·3	38·5	77·9	1·40188	42·1	41·3
66·8	1·33093	36·5	35·8	72·4	1·36611	39·3	38·6	78·0	1·40254	42·1	41·3
66·9	1·33155	36·5	35·9	72·5	1·36675	39·4	38·6	78·1	1·40321	42·2	41·4
67·0	1·33217	36·6	35·9	72·6	1·36739	39·4	38·7	78·2	1·40387	42·2	41·4
67·1	1·33278	36·6	36·0	72·7	1·36803	39·5	38·7	78·3	1·40453	42·3	41·5
67·2	1·33340	36·7	36·0	72·8	1·36867	39·5	38·8	78·4	1·40520	42·3	41·5
67·3	1·33402	36·75	36·1	72·9	1·36931	39·6	38·8	78·5	1·40586	42·4	41·6
67·4	1·33464	36·8	36·1	73·0	1·36995	39·6	38·9	78·6	1·40652	42·4	41·6
67·5	1·33526	36·85	36·2	73·1	1·37059	39·7	38·9	78·7	1·40719	42·5	41·7
67·6	1·33588	36·9	36·2	73·2	1·37124	39·7	39·0	78·8	1·40785	42·5	41·7
67·7	1·33650	36·95	36·3	73·3	1·37188	39·8	39·0	78·9	1·40852	42·6	41·8
67·8	1·33712	37·0	36·3	73·4	1·37252	39·8	39·1	79·0	1·40918	42·6	41·8
67·9	1·33774	37·0	36·4	73·5	1·37317	39·9	39·1	79·1	1·40985	42·7	41·9
68·0	1·33836	37·1	36·4	73·6	1·37381	39·9	39·2	79·2	1·41052	42·7	41·9
68·1	1·33899	37·1	36·5	73·7	1·37446	40·0	39·2	79·3	1·41118	42·8	42·0
68·2	1·33961	37·2	36·5	73·8	1·37510	40·0	39·3	79·4	1·41185	42·8	42·0

Table 46—continued.

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
79.5	1.41252	42.9	42.1	84.7	1.44779	45.4	44.5	89.9	1.48416	47.9	47.0
79.6	1.41318	42.9	42.1	84.8	1.44848	45.4	44.6	90.0	1.48486	47.9	47.0
79.7	1.41385	43.0	42.1	84.9	1.44917	45.5	44.6	90.1	1.48558	48.0	47.1
79.8	1.41452	43.0	42.2	85.0	1.44986	45.5	44.7	90.2	1.48629	48.0	47.1
79.9	1.41519	43.1	42.2	85.1	1.45055	45.6	44.7	90.3	1.48700	48.1	47.2
80.0	1.41586	43.1	42.3	85.2	1.45124	45.6	44.8	90.4	1.48771	48.1	47.2
80.1	1.41653	43.2	42.3	85.3	1.45193	45.7	44.8	90.5	1.48842	48.2	47.2
80.2	1.41720	43.2	42.4	85.4	1.45262	45.7	44.9	90.6	1.48913	48.2	47.3
80.3	1.41787	43.2	42.4	85.5	1.45331	45.8	44.9	90.7	1.48985	48.3	47.3
80.4	1.41854	43.3	42.5	85.6	1.45401	45.8	45.0	90.8	1.49056	48.35	47.4
80.5	1.41921	43.3	42.5	85.7	1.45470	45.9	45.0	90.9	1.49127	48.4	47.4
80.6	1.41989	43.4	42.6	85.8	1.45539	45.9	45.0	91.0	1.49199	48.45	47.5
80.7	1.42056	43.45	42.6	85.9	1.45609	46.0	45.1	91.1	1.49270	48.5	47.5
80.8	1.42123	43.5	42.7	86.0	1.45678	46.0	45.1	91.2	1.49342	48.5	47.6
80.9	1.42190	43.55	42.7	86.1	1.45748	46.1	45.2	91.3	1.49413	48.6	47.6
81.0	1.42258	43.6	42.8	86.2	1.45817	46.1	45.2	91.4	1.49485	48.6	47.7
81.1	1.42325	43.65	42.8	86.3	1.45887	46.2	45.3	91.5	1.49556	48.7	47.7
81.2	1.42393	43.7	42.9	86.4	1.45956	46.2	45.3	91.6	1.49628	48.7	47.8
81.3	1.42460	43.7	42.9	86.5	1.46026	46.3	45.4	91.7	1.49700	48.8	47.8
81.4	1.42528	43.8	43.0	86.6	1.46095	46.3	45.4	91.8	1.49771	48.8	47.8
81.5	1.42595	43.8	43.0	86.7	1.46165	46.35	45.5	91.9	1.49843	48.9	47.9
81.6	1.42663	43.9	43.1	86.8	1.46235	46.4	45.5	92.0	1.49915	48.9	47.9
81.7	1.42731	43.9	43.1	86.9	1.46304	46.45	45.6	92.1	1.49987	49.0	48.0
81.8	1.42798	44.0	43.2	87.0	1.46374	46.5	45.6	92.2	1.50058	49.0	48.0
81.9	1.42866	44.0	43.2	87.1	1.46444	46.55	45.7	92.3	1.50130	49.05	48.1
82.0	1.42934	44.1	43.2	87.2	1.46514	46.6	45.7	92.4	1.50202	49.1	48.1
82.1	1.43002	44.1	43.3	87.3	1.46584	46.65	45.8	92.5	1.50274	49.15	48.2
82.2	1.43070	44.2	43.3	87.4	1.46654	46.7	45.8	92.6	1.50346	49.2	48.2
82.3	1.43137	44.2	43.4	87.5	1.46724	46.7	45.8	92.7	1.50419	49.2	48.3
82.4	1.43205	44.3	43.4	87.6	1.46794	46.8	45.9	92.8	1.50491	49.3	48.3
82.5	1.43273	44.3	43.5	87.7	1.46864	46.8	45.9	92.9	1.50563	49.3	48.3
82.6	1.43341	44.4	43.5	87.8	1.46934	46.9	46.0	93.0	1.50635	49.4	48.4
82.7	1.43409	44.4	43.6	87.9	1.47004	46.9	46.0	93.1	1.50707	49.4	48.4
82.8	1.43478	44.5	43.6	88.0	1.47074	47.0	46.1	93.2	1.50779	49.5	48.5
82.9	1.43546	44.5	43.7	88.1	1.47145	47.0	46.1	93.3	1.50852	49.5	48.5
83.0	1.43614	44.6	43.7	88.2	1.47215	47.1	46.2	93.4	1.50924	49.6	48.6
83.1	1.43682	44.6	43.8	88.3	1.47285	47.1	46.2	93.5	1.50996	49.6	48.6
83.2	1.43750	44.7	43.8	88.4	1.47356	47.2	46.3	93.6	1.51069	49.6	48.7
83.3	1.43819	44.7	43.9	88.5	1.47426	47.2	46.3	93.7	1.51141	49.7	48.7
83.4	1.43887	44.8	43.9	88.6	1.47496	47.3	46.4	93.8	1.51214	49.7	48.8
83.5	1.43955	44.8	44.0	88.7	1.47567	47.3	46.4	93.9	1.51286	49.8	48.8
83.6	1.44024	44.9	44.0	88.8	1.47637	47.4	46.5	94.0	1.51359	49.8	48.8
83.7	1.44092	44.9	44.1	88.9	1.47708	47.4	46.5	94.1	1.51431	49.85	48.9
83.8	1.44161	45.0	44.1	89.0	1.47778	47.45	46.5	94.2	1.51504	49.9	48.9
83.9	1.44229	45.0	44.2	89.1	1.47849	47.5	46.6	94.3	1.51577	49.9	49.0
84.0	1.44298	45.1	44.2	89.2	1.47920	47.55	46.6	94.4	1.51649	50.0	49.0
84.1	1.44367	45.1	44.2	89.3	1.47991	47.6	46.7	94.5	1.51722	50.0	49.1
84.2	1.44435	45.15	44.3	89.4	1.48061	47.6	46.7	94.6	1.51795	50.1	49.1
84.3	1.44504	45.2	44.3	89.5	1.48132	47.7	46.8	94.7	1.51868	50.1	49.2
84.4	1.44573	45.25	44.4	89.6	1.48203	47.7	46.8	94.8	1.51941	50.2	49.2
84.5	1.44641	45.3	44.4	89.7	1.48274	47.8	46.9	94.9	1.52014	50.2	49.3
84.6	1.44710	45.35	44.5	89.8	1.48345	47.8	46.9	95.0	1.52087	50.3	49.3

In cases where the sugar solutions are not examined at the normal temperature, as often happens in practical work (in order to save the time required for cooling), the difference in volume must be allowed for. This problem has been carefully and accurately solved by Plato and his colleagues, and from the Table¹ compiled by them, the densities of sugar solutions from 0.1 to 70 per cent. sugar-content, at temperatures from 0° to 60° referred to water at 15°, may be found; this Table, however, has not hitherto been used in works laboratories. It is usual to correct the saccharometer readings either by Scheibler's Tables,² or, since these were originally based on a normal temperature of only 15°, usually by the Table (No. 47) calculated by Stammer and Sachs; this Table is referred to a temperature of 17°.5, though Sachs has recently recalculated it for a temperature of 20°.³

The use of this Table is unnecessary, however, if the Volquartz hydrometer with a correction scale⁴ is employed. In this case the mercury thread of the correction thermometer of the hydrometer does not give the actual temperature, which is of no importance in most practical determinations, but the correction corresponding to this temperature, by which the reading of the hydrometer must be increased or reduced for reference to the normal specific gravity. The hydrometer provided with Vosátka's movable scale⁵ serves a similar purpose.

A very exact method for the estimation of the specific gravity of sugar solutions, which may be used to advantage if only small quantities of material are available, depends on the employment of the pyknometer; in using this instrument, however, it is necessary to adjust the temperature to the required degree very accurately, and to perform the weighing very exactly, so that the instrument has certain disadvantages especially in cases where many determinations are to be made. Generally a tared 50 c.c. flask is used, which is filled to the mark with the liquid under examination (temperature, 17°.5 or 20°); the weight of the liquid in grams divided by 50 gives the specific gravity directly. For very exact determinations, and in special cases, *e.g.* for the determination of the specific gravity of molasses, other forms of the pyknometer, which will be described later, are used.

The employment of the well-known Mohr's balance in its various modifications, for the examination of sugar solutions, does not require special description.

¹ *Z. Ver. deut. Zuckerind.*, 1900, 50, 1110; 1903, 53, 526. See Lippmann, *Chemie der Zuckerarten*, pp. 1077 *et seq.*

² *Die Gehaltsermittlung der Zuckerlösungen durch Bestimmung des spezifischen Gewichtes derselben*, 1891.

³ Lippmann, *Chemie der Zuckerarten*, p. 1075.

⁴ *Z. Ver. deut. Zuckerind.*, 1896, 46, 392.

⁵ *Z. Zuckerind. Böhm.*, 1903, 27, 689.

Table 47.

Corrections for Saccharometer readings at different Temperatures to readings at 17°. (Sachs.)

Temperature. °C.	Degrees Brix of the solution.												
	0	5	10	15	20	25	30	35	40	50	60	70	75
	The reading obtained is to be reduced by:—												
0	0.27	0.30	0.41	0.52	0.62	0.72	0.82	0.92	0.98	1.11	1.22	1.25	1.29
5	0.23	0.30	0.37	0.44	0.52	0.59	0.65	0.72	0.75	0.80	0.88	0.91	0.94
10	0.20	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.48	0.50	0.54	0.58	0.61
11	0.18	0.23	0.26	0.28	0.31	0.34	0.36	0.39	0.41	0.43	0.47	0.50	0.53
12	0.16	0.20	0.22	0.24	0.26	0.29	0.31	0.33	0.34	0.36	0.40	0.42	0.46
13	0.14	0.18	0.19	0.21	0.22	0.24	0.26	0.27	0.28	0.29	0.33	0.35	0.39
14	0.12	0.15	0.16	0.17	0.18	0.19	0.21	0.22	0.22	0.23	0.26	0.28	0.32
15	0.09	0.11	0.12	0.14	0.14	0.15	0.16	0.17	0.16	0.17	0.19	0.21	0.25
16	0.06	0.07	0.08	0.09	0.10	0.10	0.11	0.12	0.12	0.12	0.14	0.16	0.18
17	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.06
	The reading obtained is to be increased by:—												
18	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02
19	0.06	0.08	0.08	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.08	0.06
20	0.11	0.14	0.15	0.17	0.17	0.18	0.18	0.18	0.19	0.19	0.18	0.15	0.11
21	0.16	0.20	0.22	0.24	0.24	0.25	0.25	0.25	0.26	0.26	0.25	0.22	0.18
22	0.21	0.26	0.29	0.31	0.31	0.32	0.32	0.32	0.33	0.34	0.32	0.29	0.25
23	0.27	0.32	0.35	0.37	0.38	0.39	0.39	0.39	0.40	0.42	0.39	0.36	0.33
24	0.32	0.38	0.41	0.43	0.44	0.46	0.46	0.47	0.47	0.50	0.46	0.43	0.40
25	0.37	0.44	0.47	0.49	0.51	0.53	0.54	0.55	0.55	0.58	0.54	0.51	0.48
26	0.43	0.50	0.54	0.56	0.58	0.60	0.61	0.62	0.62	0.66	0.62	0.58	0.55
27	0.49	0.57	0.61	0.63	0.65	0.68	0.68	0.69	0.70	0.74	0.70	0.65	0.62
28	0.56	0.64	0.68	0.70	0.72	0.76	0.76	0.78	0.78	0.82	0.78	0.72	0.70
29	0.63	0.71	0.75	0.78	0.79	0.84	0.84	0.86	0.86	0.90	0.86	0.80	0.78
30	0.70	0.78	0.82	0.87	0.87	0.92	0.92	0.94	0.94	0.98	0.94	0.88	0.86
35	1.10	1.17	1.22	1.24	1.30	1.32	1.33	1.35	1.36	1.39	1.34	1.27	1.25
40	1.50	1.61	1.67	1.71	1.73	1.79	1.79	1.80	1.82	1.83	1.78	1.69	1.65
50	...	2.65	2.71	2.74	2.78	2.80	2.80	2.80	2.80	2.79	2.70	2.56	2.51
60	...	3.87	3.88	3.88	3.88	3.88	3.88	3.88	3.90	3.82	3.70	3.43	3.41
70	...	5.17	5.18	5.20	5.14	5.13	5.10	5.08	5.06	4.90	4.72	4.47	4.35
80	6.62	6.59	6.54	6.46	6.38	6.30	6.26	6.06	5.82	5.50	5.33
90	8.26	8.16	8.06	7.97	7.83	7.71	7.58	7.30	6.96	6.58	6.37
100	10.01	9.87	9.72	9.56	9.39	9.21	9.03	8.64	8.22	7.76	7.42

B.—THE ESTIMATION OF SUCROSE.

I. **Gravimetric Method.**—For this estimation 26 g. of the juice (neutralised, if necessary, with acetic acid) are weighed into the tared dish, rinsed without loss into a 100 c.c. flask, and clarified with basic lead acetate solution. This addition of basic lead acetate not only effects clarification of the solution, but also causes the precipitation of optically active non-sugar substances.¹ Usually the amount of this

¹ Cf. Claassen, *Z. Ver. deut. Zuckerind.*, 1890, 40, 380, 385.

clarifying agent is so regulated that a decided excess is avoided; when a sample of the solution gives no more precipitate on the addition of another drop of basic lead acetate solution, sufficient of the latter has been added; the production of a slightly alkaline reaction may serve as a test for the same purpose. After addition of the basic lead acetate the solution is made up to the mark, mixed, filtered, and the rotation determined in a 200 mm. tube.

2. Volumetric Method.—100 c.c. of the juice are placed in a flask the neck of which is graduated to 100 and 110 c.c., and filled exactly to the second mark with basic lead acetate solution, thoroughly mixed and filtered. In the case of beetroot juice, the well-mixed solution is allowed to stand for ten to fifteen minutes before being filtered. The rotation of the filtrate in a 200 mm. tube must be increased by $\frac{1}{10}$ and then multiplied by 0.26. In this way the percentage of sugar by volume is obtained, which value, when divided by the specific gravity, gives the percentage of sugar by weight.

For manufacturing operations, Schmitz¹ has calculated auxiliary Tables from which, with simultaneous reference to the corresponding specific gravity, the content of sucrose in percentage by weight may be found without further calculation.

This Table (No. 48) is valid for the volumetric method, taking into consideration the clarification with $\frac{1}{10}$ volume of basic lead acetate solution and the varying optical rotatory power of sucrose with varying concentration.

The estimation of specific gravity may be included in the sucrose estimation by the volumetric method, the flask being weighed before and after filling with 100 c.c. of the juice.

Austrian factories make use of a short Table (No. 49) compiled by Neumann,² from which the quantities of sugar, corresponding to the polarimeter reading, may be found. As an average value for the purity of the juice (see p. 587) 90 is used as a basis, a figure which corresponds better with the conditions that now obtain than Schmitz's value, 83; the determination of the specific gravity is not necessary. The results, which are sufficiently accurate, are generally higher than those obtained by reference to Schmitz's Table, by 0.1 per cent. or more.

¹ *Z. Ver. deut. Zuckerind.*, 1880, 30, 899.

² *Z. Zuckerind. Böhm.*, 1903, 28, 165.

48

the Soleil-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)

of lead acetate solution.¹

Percentage Brix and corresponding specific gravity.										Polarimeter degrees.	Per cent. Brix from 12.5 to 20.0.	
5.5.	6.0.	6.5.	7.0.	7.5.	8.0.	8.5.	9.0.	9.5.	10.0.		Tenths of a degree.	Per cent. sugar.
1.0217.	1.0237.	1.0258.	1.0278.	1.0298.	1.0319.	1.0339.	1.0360.	1.0381.	1.0401.			
0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	1	0.1	0.03
0.56	0.56	0.56	0.56	0.55	0.55	0.55	0.55	0.55	0.55	2	0.2	0.05
0.84	0.84	0.84	0.83	0.83	0.83	0.83	0.83	0.83	0.82	3	0.3	0.08
1.12	1.12	1.11	1.11	1.11	1.11	1.11	1.10	1.10	1.10	4	0.4	0.11
1.40	1.40	1.39	1.39	1.39	1.38	1.38	1.38	1.38	1.37	5	0.5	0.13
1.68	1.67	1.67	1.67	1.66	1.66	1.66	1.66	1.65	1.65	6	0.6	0.16
1.96	1.95	1.95	1.95	1.94	1.94	1.93	1.93	1.93	1.92	7	0.7	0.19
2.24	2.23	2.23	2.22	2.22	2.22	2.21	2.21	2.20	2.20	8	0.8	0.21
2.52	2.51	2.51	2.50	2.50	2.49	2.49	2.48	2.48	2.47	9	0.9	0.24
2.80	2.79	2.79	2.78	2.78	2.77	2.76	2.76	2.75	2.75	10		
3.08	3.07	3.06	3.06	3.05	3.05	3.04	3.03	3.03	3.02	11		
3.36	3.35	3.34	3.34	3.33	3.32	3.32	3.31	3.30	3.30	12		
3.64	3.63	3.62	3.61	3.61	3.60	3.59	3.59	3.58	3.57	13		
3.92	3.91	3.90	3.89	3.88	3.88	3.87	3.86	3.85	3.85	14		
4.19	4.19	4.18	4.17	4.16	4.15	4.15	4.14	4.13	4.12	15	Per cent. Brix from 12.5 to 20.0.	
4.47	4.47	4.46	4.45	4.44	4.43	4.42	4.41	4.40	4.40	16		
4.76	4.75	4.74	4.73	4.72	4.71	4.70	4.69	4.68	4.67	17		
5.03	5.02	5.01	5.00	4.99	4.99	4.97	4.97	4.96	4.95	18	Tenths of a degree.	Per cent. sugar.
5.32	5.31	5.29	5.28	5.27	5.26	5.25	5.24	5.23	5.22	19		
	5.58	5.57	5.56	5.55	5.54	5.53	5.52	5.51	5.50	20		
	5.86	5.85	5.84	5.83	5.82	5.81	5.79	5.78	5.77	21	0.1	0.03
		6.13	6.12	6.11	6.09	6.08	6.07	6.06	6.05	22	0.2	0.05
		6.41	6.40	6.38	6.37	6.36	6.35	6.33	6.32	23	0.3	0.08
			6.67	6.66	6.65	6.64	6.62	6.61	6.60	24	0.4	0.11
				6.94	6.93	6.91	6.90	6.89	6.87	25	0.5	0.13
				7.22	7.20	7.19	7.17	7.16	7.15	26	0.6	0.16
					7.48	7.46	7.45	7.44	7.42	27	0.7	0.18
					7.76	7.74	7.73	7.71	7.70	28	0.8	0.21
						8.02	8.00	7.99	7.97	29	0.9	0.23
							8.28	8.26	8.25	30		
							8.55	8.54	8.52	31		
							8.83	8.81	8.80	32		
								9.08	9.07	33		
									9.35	34		
									9.62	35		
										36		
										37		
										38.		
										39		

¹ Z. Ver. deut. Zuckerind., 1880, 30, 899.

Table

Table giving the content of Sucrose in Percentage Weight for
and with regard to the variable Specific

With addition of $\frac{1}{10}$ volume

Per cent. Brix from 0.5 to 12.0.		Polarimeter degrees.	Percentage Brix and corresponding specific gravity.									
Tenths of a degree.	Per cent. sugar.		10.5. 1.0422.	11.0. 1.0443.	11.5. 1.0464.	12.0. 1.0485.	12.5. 1.0506.	13.0. 1.0528.	13.5. 1.0549.	14.0. 1.0570.	14.5. 1.0592.	15.0. 1.0613.
0.1	0.03	1	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
0.2	0.06	2	0.55	0.55	0.55	0.55	0.54	0.54	0.54	0.54	0.54	0.54
0.3	0.08	3	0.82	0.82	0.82	0.82	0.82	0.81	0.81	0.81	0.81	0.81
0.4	0.11	4	1.10	1.10	1.09	1.09	1.09	1.09	1.08	1.08	1.08	1.08
0.5	0.14	5	1.37	1.37	1.36	1.36	1.36	1.36	1.35	1.35	1.35	1.35
0.6	0.17	6	1.64	1.64	1.64	1.64	1.63	1.63	1.62	1.62	1.62	1.62
0.7	0.19	7	1.92	1.91	1.91	1.91	1.90	1.90	1.89	1.89	1.89	1.88
0.8	0.22	8	2.19	2.19	2.18	2.18	2.18	2.17	2.17	2.16	2.16	2.15
0.9	0.25	9	2.47	2.46	2.46	2.45	2.45	2.44	2.44	2.43	2.43	2.42
Per cent. Brix from 6.0 to 12.0.		10	2.74	2.74	2.73	2.73	2.72	2.71	2.71	2.70	2.70	2.69
		11	3.02	3.01	3.00	3.00	2.99	2.99	2.98	2.97	2.97	2.96
		12	3.29	3.28	3.28	3.27	3.26	3.26	3.25	3.24	3.24	3.23
		13	3.56	3.56	3.55	3.54	3.54	3.53	3.52	3.51	3.51	3.50
		14	3.84	3.83	3.82	3.82	3.81	3.80	3.79	3.78	3.78	3.77
Tenths of a degree.	Per cent. sugar.	15	4.11	4.11	4.10	4.09	4.08	4.07	4.06	4.06	4.05	4.04
		16	4.39	4.38	4.37	4.36	4.35	4.34	4.33	4.33	4.32	4.31
		17	4.66	4.65	4.64	4.63	4.62	4.62	4.61	4.60	4.59	4.58
		18	4.93	4.93	4.91	4.91	4.90	4.89	4.88	4.87	4.86	4.85
		19	5.21	5.20	5.19	5.18	5.17	5.16	5.15	5.14	5.13	5.12
0.1	0.03	20	5.49	5.47	5.46	5.45	5.44	5.43	5.42	5.41	5.40	5.39
		21	5.76	5.75	5.74	5.73	5.71	5.70	5.69	5.68	5.67	5.66
		22	6.03	6.02	6.01	6.00	5.99	5.97	5.96	5.95	5.94	5.93
		23	6.31	6.30	6.28	6.27	6.26	6.24	6.23	6.22	6.21	6.20
		24	6.58	6.57	6.56	6.54	6.53	6.52	6.50	6.49	6.48	6.46
0.5	0.14	25	6.86	6.84	6.83	6.82	6.80	6.79	6.78	6.76	6.75	6.73
		26	7.13	7.12	7.10	7.09	7.07	7.06	7.05	7.03	7.02	7.00
		27	7.41	7.39	7.38	7.36	7.35	7.33	7.32	7.30	7.29	7.27
		28	7.68	7.66	7.65	7.63	7.62	7.60	7.59	7.57	7.56	7.54
		29	7.96	7.94	7.92	7.91	7.89	7.87	7.86	7.84	7.83	7.81
0.6	0.17	30	8.23	8.21	8.20	8.18	8.16	8.15	8.13	8.11	8.10	8.08
		31	8.50	8.49	8.47	8.45	8.44	8.42	8.40	8.39	8.37	8.35
		32	8.78	8.76	8.74	8.73	8.71	8.69	8.67	8.66	8.64	8.62
		33	9.05	9.03	9.02	9.00	8.98	8.96	8.94	8.93	8.91	8.89
		34	9.33	9.31	9.29	9.27	9.25	9.23	9.22	9.20	9.18	9.16
0.7	0.19	35	9.60	9.58	9.56	9.54	9.53	9.51	9.49	9.47	9.45	9.43
		36	9.88	9.86	9.84	9.82	9.80	9.78	9.76	9.74	9.72	9.70
		37	10.15	10.13	10.11	10.09	10.07	10.05	10.03	10.01	9.99	9.97
		38		10.40	10.38	10.36	10.34	10.32	10.30	10.28	10.26	10.24
		39		10.68	10.66	10.64	10.61	10.59	10.57	10.55	10.53	10.51

48—continued.

the Soleil-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)

of lead acetate solution.¹

Percentage Brix and corresponding specific gravity.										Polarimeter degrees.	Per cent. Brix from 12.5 to 20.0.	
15.5. 1.0635.	16.0. 1.0657.	16.5. 1.0678.	17.0. 1.0700.	17.5. 1.0722.	18.0. 1.0744.	18.5. 1.0766.	19.0. 1.0788.	19.5. 1.0811.	20.0. 1.0833.		Tenths of a degree.	Per cent. sugar.
0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.26	1	0.1	0.03
0.54	0.54	0.54	0.53	0.53	0.53	0.53	0.53	0.53	0.53	2	0.2	0.05
0.81	0.80	0.80	0.80	0.80	0.80	0.80	0.79	0.79	0.79	3	0.3	0.08
1.08	1.07	1.07	1.07	1.07	1.06	1.06	1.06	1.06	1.06	4	0.4	0.11
1.34	1.34	1.34	1.34	1.33	1.33	1.33	1.32	1.32	1.32	5	0.5	0.13
1.61	1.61	1.61	1.60	1.60	1.60	1.59	1.59	1.59	1.58	6	0.6	0.16
1.88	1.88	1.87	1.87	1.86	1.86	1.86	1.85	1.85	1.85	7	0.7	0.19
2.15	2.15	2.14	2.14	2.13	2.13	2.12	2.12	2.12	2.11	8	0.8	0.21
2.42	2.41	2.41	2.40	2.40	2.39	2.39	2.38	2.38	2.37	9	0.9	0.24
2.69	2.68	2.68	2.67	2.67	2.66	2.65	2.65	2.64	2.64	10		
2.95	2.95	2.94	2.94	2.93	2.92	2.92	2.91	2.91	2.90	11		
3.22	3.22	3.21	3.20	3.20	3.19	3.18	3.18	3.17	3.17	12		
3.49	3.49	3.48	3.47	3.46	3.46	3.45	3.44	3.44	3.43	13		
3.76	3.75	3.75	3.74	3.73	3.72	3.72	3.71	3.70	3.69	14		
4.03	4.02	4.02	4.01	4.00	3.99	3.98	3.97	3.97	3.96	15	Per cent. Brix from 12.5 to 20.0.	
4.30	4.29	4.28	4.27	4.26	4.26	4.25	4.24	4.23	4.22	16		
4.57	4.56	4.55	4.54	4.53	4.52	4.51	4.50	4.49	4.48	17	Tenths of a degree.	Per cent. sugar.
4.84	4.83	4.82	4.81	4.80	4.79	4.78	4.77	4.76	4.75	18		
5.11	5.10	5.09	5.08	5.06	5.05	5.04	5.03	5.02	5.01	19		
5.38	5.36	5.35	5.34	5.33	5.32	5.31	5.30	5.29	5.28	20		
5.65	5.63	5.62	5.61	5.60	5.59	5.58	5.56	5.55	5.54	21	0.1	0.03
5.91	5.90	5.89	5.88	5.87	5.85	5.84	5.83	5.82	5.80	22	0.2	0.05
6.18	6.17	6.16	6.14	6.13	6.12	6.11	6.09	6.08	6.07	23	0.3	0.08
6.45	6.44	6.43	6.41	6.40	6.39	6.37	6.36	6.35	6.33	24	0.4	0.11
6.72	6.71	6.69	6.68	6.67	6.65	6.64	6.63	6.61	6.60	25	0.5	0.13
6.99	6.97	6.96	6.95	6.93	6.92	6.90	6.89	6.88	6.86	26	0.6	0.16
7.26	7.24	7.23	7.21	7.20	7.18	7.17	7.15	7.14	7.13	27	0.7	0.18
7.53	7.51	7.50	7.48	7.47	7.45	7.44	7.42	7.40	7.39	28	0.8	0.21
7.80	7.78	7.77	7.75	7.73	7.72	7.70	7.68	7.67	7.65	29	0.9	0.23
8.06	8.05	8.03	8.02	8.00	7.98	7.97	7.95	7.93	7.92	30		
8.33	8.32	8.30	8.28	8.27	8.25	8.23	8.21	8.20	8.18	31		
8.60	8.58	8.57	8.55	8.53	8.51	8.50	8.48	8.46	8.45	32		
8.87	8.85	8.84	8.82	8.80	8.78	8.76	8.75	8.73	8.71	33		
9.14	9.12	9.10	9.09	9.07	9.05	9.03	9.01	8.99	8.97	34		
9.41	9.39	9.37	9.35	9.34	9.31	9.30	9.28	9.26	9.24	35		
9.68	9.66	9.64	9.62	9.60	9.58	9.56	9.54	9.52	9.50	36		
9.95	9.93	9.91	9.89	9.87	9.85	9.83	9.81	9.79	9.77	37		
10.22	10.20	10.18	10.15	10.13	10.11	10.09	10.07	10.05	10.03	38		
10.49	10.46	10.44	10.42	10.40	10.38	10.36	10.34	10.32	10.29	39		

¹ Z. Ver. deut. Zuckerind., 1880, 30, 899.

48-- continued.

the Soliel-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)

of lead acetate solution.¹

Percentage Brix and corresponding specific gravity.													Polarimeter degrees.	Percent. Brix from 23.0 to 24.0.	
18.0	18.5	19.0	19.5	20.0	20.5	21.0	21.5	22.0	22.5	23.0	23.5	24.0		Tenths of a degree.	Per cent. sugar.
1.0744	1.0766	1.0788	1.0811	1.0833	1.0855	1.0878	1.0900	1.0923	1.0946	1.0969	1.0992	1.1015			
10.64	10.62	10.60	10.58	10.56	10.54	10.52	10.49	10.47	10.45	10.43	10.41	10.38	40		
10.91	10.89	10.87	10.85	10.82	10.80	10.78	10.76	10.74	10.71	10.69	10.67	10.65	41	0.1	0.03
11.18	11.16	11.13	11.11	11.09	11.07	11.04	11.02	11.00	10.97	10.95	10.93	10.90	42	0.2	0.05
11.45	11.42	11.40	11.38	11.35	11.33	11.31	11.28	11.26	11.24	11.21	11.19	11.17	43	0.3	0.08
11.71	11.69	11.66	11.64	11.62	11.59	11.57	11.55	11.52	11.50	11.47	11.45	11.42	44	0.4	0.10
11.98	11.96	11.93	11.91	11.88	11.86	11.83	11.81	11.78	11.76	11.73	11.71	11.69	45	0.5	0.13
12.25	12.22	12.20	12.17	12.15	12.12	12.09	12.07	12.05	12.02	12.00	11.97	11.94	46	0.6	0.16
12.51	12.49	12.46	12.44	12.41	12.39	12.36	12.33	12.31	12.28	12.26	12.23	12.21	47	0.7	0.18
12.78	12.75	12.73	12.70	12.67	12.65	12.62	12.60	12.57	12.54	12.52	12.49	12.47	48	0.8	0.21
13.05	13.02	12.99	12.97	12.94	12.91	12.88	12.86	12.83	12.81	12.78	12.75	12.73	49	0.9	0.23
13.31	13.29	13.26	13.23	13.20	13.18	13.15	13.12	13.09	13.07	13.04	13.01	12.99	50		
13.58	13.55	13.52	13.50	13.47	13.44	13.41	13.39	13.36	13.33	13.30	13.27	13.25	51		
13.85	13.82	13.79	13.76	13.73	13.70	13.68	13.65	13.62	13.59	13.56	13.53	13.51	52		
14.11	14.08	14.05	14.03	14.00	13.97	13.94	13.91	13.88	13.85	13.82	13.79	13.77	53		
14.38	14.35	14.32	14.29	14.26	14.23	14.20	14.17	14.14	14.11	14.08	14.04	14.02	54	Percent. Brix from 23.5 to 24.0.	
14.65	14.62	14.59	14.56	14.53	14.50	14.47	14.44	14.41	14.38	14.35	14.32	14.29	55		
14.91	14.88	14.85	14.82	14.79	14.76	14.73	14.70	14.67	14.64	14.61	14.58	14.55	56		
15.18	15.15	15.12	15.09	15.06	15.02	14.99	14.96	14.93	14.90	14.87	14.84	14.81	57		
15.45	15.42	15.38	15.35	15.32	15.29	15.26	15.23	15.19	15.16	15.13	15.10	15.07	58		
15.71	15.68	15.65	15.62	15.58	15.55	15.52	15.49	15.46	15.42	15.39	15.36	15.33	59		
15.98	15.95	15.92	15.88	15.85	15.82	15.78	15.75	15.72	15.69	15.65	15.62	15.59	60		
16.25	16.21	16.18	16.15	16.11	16.08	16.05	16.01	15.98	15.95	15.91	15.88	15.85	61	0.1	0.03
16.52	16.48	16.45	16.41	16.38	16.35	16.31	16.28	16.24	16.21	16.18	16.14	16.11	62	0.2	0.05
16.78	16.75	16.71	16.68	16.64	16.61	16.57	16.54	16.51	16.47	16.44	16.40	16.37	63	0.3	0.08
17.05	17.01	16.98	16.94	16.91	16.87	16.84	16.80	16.77	16.73	16.70	16.66	16.63	64	0.4	0.10
17.32	17.28	17.24	17.21	17.17	17.14	17.10	17.07	17.03	17.00	16.96	16.92	16.89	65	0.5	0.13
	17.55	17.51	17.47	17.44	17.40	17.37	17.33	17.29	17.26	17.22	17.19	17.15	66	0.6	0.16
	17.81	17.78	17.74	17.70	17.67	17.63	17.59	17.56	17.52	17.48	17.45	17.41	67	0.7	0.18
		18.04	18.00	17.97	17.93	17.89	17.86	17.82	17.78	17.74	17.71	17.67	68	0.8	0.21
		18.31	18.27	18.23	18.19	18.16	18.12	18.08	18.04	18.00	17.97	17.93	69	0.9	0.23
			18.53	18.50	18.46	18.42	18.38	18.35	18.31	18.27	18.23	18.19	70		
				18.76	18.72	18.68	18.65	18.61	18.57	18.53	18.49	18.45	71		
				19.03	18.99	18.95	18.91	18.87	18.83	18.79	18.75	18.71	72		
					19.25	19.21	19.17	19.13	19.09	19.05	19.01	18.97	73		
					19.52	19.48	19.44	19.40	19.35	19.31	19.27	19.23	74		
						19.78	19.74	19.70	19.66	19.62	19.57	19.53	75		
							20.00	19.96	19.92	19.88	19.84	19.80	76		
							20.27	20.22	20.18	20.14	20.10	20.06	77		
								20.49	20.45	20.40	20.36	20.32	78		
								20.75	20.71	20.66	20.62	20.58	79		
									20.97	20.93	20.88	20.84	80		

¹ Z. Ver. deut. Zuckerind., 1880, 30, 899.

Table 49.

Table giving the Percentage of Sugar corresponding to the Polarimeter Readings for solutions clarified with $\frac{1}{10}$ volume of basic lead acetate. (Neumann.)

Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.
1	0.29	26	7.22	51	13.75	76	19.90
2	0.57	27	7.48	52	14.01	77	20.14
3	0.86	28	7.75	53	14.26	78	20.37
4	1.14	29	8.02	54	14.51	79	20.61
5	1.42	30	8.29	55	14.76	80	20.84
6	1.71	31	8.56	56	15.01	81	21.07
7	1.99	32	8.82	57	15.26	82	21.30
8	2.27	33	9.09	58	15.51	83	21.53
9	2.55	34	9.35	59	15.76	84	21.77
10	2.83	35	9.61	60	16.01	85	22.01
11	3.11	36	9.87	61	16.26	86	22.25
12	3.39	37	10.14	62	16.51	87	22.49
13	3.67	38	10.40	63	16.76	88	22.73
14	3.94	39	10.66	64	17.01	89	22.97
15	4.22	40	10.92	65	17.26	90	23.21
16	4.49	41	11.18	66	17.51	91	23.44
17	4.76	42	11.44	67	17.76	92	23.67
18	5.04	43	11.70	68	18.00	93	23.90
19	5.31	44	11.96	69	18.24	94	24.13
20	5.59	45	12.22	70	18.48	95	24.36
21	5.86	46	12.48	71	18.72	96	24.59
22	6.13	47	12.74	72	18.96	97	24.82
23	6.41	48	12.99	73	19.19	98	25.05
24	6.68	49	13.24	74	19.43	99	25.28
25	6.95	50	13.49	75	19.68	100	25.51

Fractions of a degree.	Readings in whole degrees.		
	1 to 30.	31 to 65.	66 to 100.
0.1	0.03	0.03	0.02
0.2	0.05	0.05	0.05
0.3	0.08	0.08	0.07
0.4	0.11	0.10	0.09
0.5	0.14	0.13	0.12
0.6	0.16	0.15	0.14
0.7	0.19	0.18	0.17
0.8	0.22	0.20	0.19
0.9	0.25	0.23	0.21

C.—ESTIMATION OF WATER AND NON-SUGAR: PURITY QUOTIENT.

As already mentioned, Brix's hydrometer only indicates the "apparent" percentage of dry substance. To find the "true" content it is necessary to carry out a direct estimation of the amount of water in the juice.

If the material under examination is diffusion juice, etc., Claassen's method¹ may be used. For this purpose 12-15 g. of the sample are thoroughly mixed in a glass dish with 80 g. of sand, the mixture being dried first at 70° for two hours, and then *in vacuo* at 103°-105° for five to six hours, by which time all the water should have been expelled.

In the case of thin juice, etc., half the above-mentioned quantity of sand generally suffices. The method of weighing a dish containing 20-25 g. of quartz sand and a glass rod, adding 10-20 c.c. of the juice, weighing again, then mixing the sand and juice thoroughly, and drying at 105°-110° until the weight is constant, does not give satisfactory results, especially in the case of diffusion juice, etc.

The difference between the amounts of dry substance and the sugar, or between 100 and the sum of sugar and water, represents the amount of the total non-sugar substances.

By "*Purity Quotient*" is understood the percentage of sucrose in the dry substance, and a knowledge of this value, which is always independent of the dilution, is of great importance for judging the manufacturing value of liquors that contain sucrose. If the percentage of sucrose found by the analysis of such a liquor is multiplied by 100 and divided by the apparent content of dry substance, the apparent coefficient of purity is obtained; the true quotient of purity is obtained by dividing by the true content of dry substance found by means of the estimation of the water.

With regard to the quotient of purity of beetroot juice, the usual method of estimating the purity with the expressed juice gives very untrustworthy values, since, according to the intensity and duration of pressing, and the way in which the material to be pressed is prepared (especially in respect of the degree of disintegration), extraordinarily variable results are obtained; this method has been used only in default of a better, and is still mostly employed in cases where importance is attached to the determination of this quotient. In such cases, however, the method worked out by Krause² is certainly to be preferred. This method is carried out as follows³:—104.2 g. (*i.e.* four times the normal weight) of homogeneous beetroot pulp (which may

¹ *Z. Ver. deut. Zuckerind.*, 1910, 60, 323.

² *Oesterr.-Ungar. Zeitschr.*, 1899, 28, 486.

³ *Cl. Oesterr.-Ungar. Zeitschr.*, 1901, 30, 671.

be finely triturated if desired, or as coarse as it is obtained with a hand grater with 5 mm. holes) are placed in a flask graduated to 402.8 c.c. (Mohr's), the residue being rinsed into the flask with water at a temperature of 90°. The flask is filled to three-quarters of its capacity with hot water, and at once placed in a water-bath at 90°, where it is left for twenty minutes with occasional shaking to remove air bubbles. The latter are broken by addition of a very small quantity of ether (the flask being removed for a moment from the bath). The flask is then filled to about 1 c.c. above the mark with water at 90°, allowed to stand for ten minutes in the bath at 90°, and finally, a few drops of ether are added if necessary. A thermometer is now inserted in the flask, and the latter is cooled, preferably at once, to 17°.5. The contents of the flask are then made up to the mark, thoroughly mixed, and filtered through a fine wire-gauze funnel in the apex of which some cotton- or glass-wool is placed. The filtrate is carefully poured again on the pulp in the funnel in order to remove froth, any further portion of which is removed with filter paper. The clear filtrate is placed in a cylinder of 200-300 c.c. capacity, and tested with Krause's hydrometer.¹ This instrument has a thermometer and temperature-correction, and two scales on its flat stem. One of these scales gives the degrees Brix of the diluted solution; the other (graduated empirically) gives converted degrees Brix corresponding to the soluble (apparent) dry substance of the original beetroot pulp (referred to the normal weight). Hence, with this instrument, value in degrees Brix of the original beetroot juice is ascertained, and if 100 c.c. of the juice are then polarised in the usual way, the (apparent) purity of the beetroot can be calculated with uniformly trustworthy results. In this respect Krause's method is much superior to the old method in which expressed juice is employed, and as Herrmann² has justly observed, it is especially advantageous in cases where a definite basis is required, *e.g.*, in making comparative experiments on different methods of juice extraction. Whether, on the other hand, the purity of the juice as found by Krause's method bears a constant relation to the quotient of purity of the diffusion juice as found by direct estimation appears doubtful, although, according to Herrmann,³ the results furnish a valuable control in many cases. In the opinion of many, however, the quotient of the beetroot juice is of no practical importance, and its determination is so much useless labour. Of course, Krause's method must not be used in the case of beetroots of such a nature that the method of hot aqueous digestion for the estimation of sugar does not appear suitable.

¹ Krause's hydrometer is supplied by H. Kappeller, 13 Franzensgasse, Vienna.

² *Bull. Assoc. Chim. Sucr.*, 1904, 21, 988.

³ *Z. Ver. deut. Zuckerind.*, 1903, 53, 485; *cf.* also Sigmond, *Oesterr.-Ungar. Zeitschr.*, 1905, 34, 45.

The use of Tables of coefficients for the conversion of apparent into true purity by means of average values is not to be recommended, especially since the values in question appear to vary according to local conditions and must therefore be determined empirically for the products of every factory and also be checked from time to time. According to Claassen,¹ comparisons between the purities of the diffusion juice and of the various factory products are quite worthless if the apparent quotients are taken as the basis; all such calculations should be made on the basis of the true purities.

Since the frequent calculation of the quotient of purity occupies much time, various Tables have been compiled which give the purity quotients for given proportions of dry substance and sugar directly. The "Proell Calculating Table" has proved very useful, and is applicable to all cases in which multiplication and division occur.²

The so-called "Stammer's value,"³ which is used by many workers for valuing the manufacturing material, is obtained by multiplying the sugar-content by the apparent or true coefficient of purity and dividing the product by 100.

D.—ESTIMATION OF ASH.

The estimation of ash in saccharine liquids by direct incineration is very slow and tedious. The solution must first be evaporated, then carbonised, the bulky mass of charcoal repeatedly washed with water and then burnt, and the remaining insoluble ash estimated together with the ignited residue of soluble ash in the filtrate. In this way the total amount of ash, which consists chiefly of carbonates, is obtained.

The following much more expeditious sulphate method, due to C. Scheibler, is therefore generally used. In the case of beetroot juice, thin juice, and similar solutions, a quantity, containing about 2-3 g. of dry substance, is weighed into a shallow platinum dish, evaporated to dryness, moistened thoroughly with pure, concentrated sulphuric acid, and gradually heated over a burner until the contents of the dish are carbonised, the mass being stirred with a platinum wire during the heating. The charred mass is then incinerated in a platinum or fire-clay muffle at a dull red heat (about 700°), so that fusion of the ash,⁴ which must be quite powdery and show no alkalinity to litmus on solution in water, is avoided. 10 per cent. is deducted from the weight of ash obtained, in order (according to Scheibler's original estimations with raw sugars) to compensate for the greater molecular weight of the sulphates as compared with that of the carbonates originally present;

¹ *Z. Ver. deut. Zuckerind.*, 1910, 60, 323.

² This Table is published in pocket-book form by Julius Springer, Berlin.

³ Stammer, *Lehrbuch d. Zuckerfabrikation*, 2nd ed., p. 143.

⁴ Cf. Schrefeld, *Z. Ver. deut. Zuckerind.*, 1897, 47, 560; Herzog, *ibid.*, 1899, 49, 534.

though this correction cannot be universally accurate even for raw sugars, it is, however, always used for all sugar-containing products.

The inclusion of the carbonic acid, formed by the oxidation of the organic acids, in the calculation of the "carbonate ash" instead of deducting it and adding it to the organic matter is incorrect, although it is the universal practice.

A more rational method of incineration with the addition of quartz sand, which has been suggested by Alberti and Hempel,¹ satisfies all requirements, both for scientific and technical purposes, since it permits of the determination of the inorganic matter actually present. It has not yet, however, been used in practical work, since the customary, older method is still required in commercial analyses.

If the ash-content is deducted from the total non-sugar-content, the difference represents the organic non-sugar-content; in commercial work no distinction is made between the total ash-content and that of the actual salts.

E.—ESTIMATION OF INVERT SUGAR.

For this estimation Claassen's titration method,² which depends on the principles explained above (p. 587), is used.

100 c.c. of the juice are treated with 10 c.c. of basic lead acetate solution, thoroughly mixed and filtered; 55 c.c. of the filtrate are transferred to a 250 c.c. flask and carefully freed from lead with a solution of sodium carbonate. The contents of the flask are made up to the mark, mixed and filtered; 50 c.c. of this filtrate (= 10 c.c. of the original juice) are boiled with 10 c.c. of Fehling's solution in the usual way, and titrated with 0.2 per cent. invert sugar solution until all the copper is precipitated. The titration of the Fehling's solution is carried out as follows:—10 c.c. of the Fehling's solution are treated with 50 c.c. of a solution containing 1 g. of pure sugar (corresponding approximately to the amount of sugar in 10 c.c. of raw juice), the whole boiled and then titrated with the 0.2 per cent. invert sugar solution. The difference between the numbers of cubic centimetres used in this titration and in the titration with the juice, multiplied by 0.002, gives the amount of invert sugar in 10 c.c. of the juice. This quantity, multiplied by 10, gives the percentage content.

The approximate estimation of invert sugar in beetroot juices and thin juices may be carried out as follows³:—Portions of 5 c.c. each of Fehling's solution are placed in a series of test tubes and 1, 2, 3, etc., c.c. respectively of the juice under examination are added. The contents of the tubes are then boiled for a short time and filtered

¹ *Z. Ver. deut. Zuckerind.*, 1891, 41, 743.

² *Deutsche Zuckerindustrie*, 1893, p. 338.

³ *Korrespondenzblatt*, 1892, No. 4.

at once. The filtrates are acidified strongly with acetic acid, and then treated with a solution of potassium ferrocyanide. The liquids which still contain copper give a brown precipitate or coloration, and the number of cubic centimetres of sugar solution required to precipitate all the copper is represented by the mean of the two consecutive tests, of which one gives a precipitate or coloration with potassium ferrocyanide, whilst the other does not. In making the calculation, it is assumed that 5 c.c. of Fehling-Soxhlet solution corresponds to 0.02 g. (more accurately 0.023 g.) of invert sugar; if a cubic centimetres of juice are employed, then:—

$$a : 0.02 = 100 : x,$$

$$\text{and } x (\text{Percentage of Invert Sugar}) = \frac{100 \times 0.02}{a}.$$

F.—ESTIMATION OF ALKALINITY, ACIDITY, AND COAGULABILITY.

Alkalinity.—For the estimation of alkalinity, $N/28$ acid is used; 1 c.c. of this solution = 0.01 g. CaO. If 10 c.c. of the juice are used in the estimation, the number of cubic centimetres of acid required gives the alkalinity directly expressed in tenths per cent. of calcium oxide by volume of juice, according to the prevailing custom. Sensitive litmus tincture is often used as indicator; it keeps much better if a few small pieces of thymol are added to it. Pure phenolphthalein, however, is the best indicator.¹ In comparative experiments the same indicator must be used throughout, since, as is well known, the different indicators do not give the same results, and, moreover, the colour of the juice often renders the end-point very indistinct.

In the presence of carbonates, methyl orange is used as the indicator, although, like many other indicators, it has not been employed very much in the sugar industry. For the estimation of free alkali in beetroot and sugar juice, Cortrait² recommends iodide of starch as an indicator which changes sharply and exactly from deep blue to colourless, and is not affected by ammonia or carbonates.

As the result of careful experiments, Pellet³ recommends the use of sized paper soaked in "sensitive" litmus tincture as indicator. The "sensitive" litmus paper must give a perceptible reaction with $N/100$ sodium hydroxide, and according to Pellet, it is far superior under all conditions, even in the case of juice containing free sulphurous acid,

¹ Cf. Herzfeld, *Z. Ver. deut. Zuckerind.*, 1893, 43, 631.

² *Z. Ver. deut. Zuckerind.*, 1897, 47, 31.

³ *Sucrierie Belge*, 1898, 26, 91; *Bull. Assoc. Chim. Sucr.*, 1901, 18, 693; *ibid.*, 1905, 23, 620; 1907, 25, 392.

to all the other indicators that have been proposed. In this opinion, however, Pellet stands practically alone.

Lime.—The most accurate, rapid method consists in precipitating the calcium with ammonium oxalate and titrating the calcium oxalate with potassium permanganate. This method is specially suited for technical purposes. It is to be borne in mind, however, that after standing for some time at a moderate temperature, organic compounds may be precipitated from the solution treated with ammonium oxalate and acetic acid; this fact is of importance since such compounds may be subsequently oxidised by the permanganate.

Acidity.—According to Herzfeld¹ the estimation of acidity is chiefly required for diffusion juice and similar liquids. For the determination 25 c.c. of the juice are diluted with so much phenolphthalein-neutral water (for the preparation of which see below in connection with the estimation of the alkalinity of raw sugar, p. 615) that the transition tint may be easily recognised, and titrated with an $N/28$ solution of sodium hydroxide; the number of cubic centimetres of alkali required is multiplied by 4, and the product, representing the acidity, expressed in terms of hundredths of 1 per cent. of calcium oxide.

Coagulability.—Herzfeld's method² for estimating the so-called coagulability of crude juice is as follows:—25 c.c. of the juice together with 3 drops of glacial acetic acid are introduced into a graduated test tube of about 18 mm. diameter. The whole is heated in a water-bath at 80° - 85° for three minutes, and allowed to stand for three hours at the ordinary temperature. The volume of the precipitate in cubic centimetres is then read and multiplied by 4.

G.—ESTIMATION OF COLOUR.

For this purpose, Stammer's colorimeter or Gröger's³ improved colour scale is used. Since, however, such estimations are rarely required, it is sufficient to follow the directions supplied with each apparatus for its adjustment and use. Stammer's colorimeter is fully described in the section on "Mineral Oils," this Vol., p. 25.

2. WASTE-WATER, WASH-WATER, ETC.

The waste-waters, etc., obtained in the extraction of the juice, and the so-called return-waters of the diffusion process are generally examined for gravity (with observance of all necessary precautions) directly after sampling, and the sucrose-content (found by determining the rotation of 100 c.c. clarified with 5-10 c.c. of basic lead acetate

¹ *Deutsche Zuckerindustrie*, 1909, 34, 293, 973.

² *Loc. cit.*

³ *Oesterr.-Ungar. Zeitschr.*, 1903, p. 62.

solution), the content of invert sugar, the acidity and the coagulability are estimated in the same way as in the case of crude juice.

The examination of wash-waters from filters, filter-presses, etc., is generally confined to the estimation of the sucrose-content. If the amount of sucrose is too small for direct estimation, 500 c.c. of the water are treated with a few drops of sodium carbonate solution or milk of lime, concentrated on the water-bath to about 50 c.c., rinsed into a 100 c.c. flask, clarified with basic lead acetate solution, made up to 100 c.c., mixed, filtered, and the rotation determined. The polarimetric reading is multiplied by 0.26, and divided by 5, the result representing the percentage of sucrose by volume.

If accurate estimations of the proportions of water and salt are required, 100 c.c. of the liquid, for each estimation, are concentrated on the water-bath to a small bulk, the rest of the analysis being carried out as described above.

For the factory control of the treatment of the wash-waters, such as are obtained, for instance, with filter-presses or filters, special hydrometers are used, which, since the samples of wash-waters are always taken at a temperature of 60° - 80° , are graduated for a certain high temperature, thus rendering the cooling of the liquid to the normal temperature unnecessary. The divisions of the scale range from 0° to 5° Brix, and they are sufficiently far apart to allow of the accurate reading of the instrument to tenths of a degree Brix. A popular form of hydrometer, also, is one which is adjusted for the normal temperature of $17^{\circ}5$, and has a scale ranging from -5° to $+5^{\circ}$ Brix. This instrument sinks to the zero point in pure water at $17^{\circ}5$, to -5° in pure water at 70° , to $+5^{\circ}$ in 5 per cent. solution of sucrose at $17^{\circ}5$, and to the zero point in 5 per cent. solution of sucrose at 70° .

With Langen's hydrometer, the completion of the washing process may be observed with liquid of any temperature. It contains a thermometer ranging from 30° to 70° , and its scale is such that at every point to which the hydrometer sinks in pure water at 30° to 70° , the same number is registered as on the temperature scale. In the case of pure water, therefore, both readings are the same throughout; with wash-waters, on the contrary, the difference between the two readings is the greater, the greater the content of dissolved substances. Hence in the initial stage of washing a considerable difference is generally observed which gradually decreases with the duration of washing, until finally, after complete extraction, both readings agree, thereby indicating the complete removal of soluble matter.

The defecation water and the condensation water are, as a rule, only examined qualitatively for sucrose by means of the α -naphthol reaction (after filtration and removal of fat with petroleum spirit).

3. EXTRACTED SLICES AND PRESSED SLICES: DRY SLICES AND SUGAR SLICES.

(a) In the case of the examination of wet extracted slices, a method suggested by Stammer¹ is considered sufficient in many factories for the purposes of daily working control. Any desired quantity of the shredded pulp is treated with a small quantity of basic lead acetate solution, thoroughly mixed and filtered, and the rotation of the filtrate determined in a 400 mm. tube. By multiplying the polarimeter reading by 0.13 the percentage of sucrose in the juice of the pulp is obtained; the small volume of the basic lead acetate solution added may be neglected. If it is desired to avoid the preparation of shredded pulp the rotation may also be determined on the juice expressed from the minced slices, since with the small quantities of sucrose under consideration small differences in the fibre- or juice-content cause no appreciable error. Sufficient basic lead acetate solution is added, drop by drop, to the juice to render the precipitate flocculent, and the solution is then filtered. The polarimeter reading divided by 4 gives the content of sucrose.

It is obvious that such a method, although having much to recommend it by reason of its simplicity, cannot claim any high degree of accuracy, especially as it is very difficult to obtain a representative sample. Where exact values are required, applicable for example to the calculation of loss, Claassen² recommends the examination of the pressed slices by hot aqueous digestion of the coarse pulp, and also, the estimation of the sucrose-content of the press-water in the usual way; average samples of this press-water are best obtained by means of one of the well-known dropping devices. Besides Pellet's method, that recommended by Herzfeld³ and by Sachs-Le Docte⁴ can be applied to the extracted beet-root slices as well as to the fresh slices. For this purpose it is best to employ freshly drawn individual samples, 60 g. of which are digested with 177 c.c. of diluted solution of basic lead acetate, the rotation being determined in a 200 mm. tube, or, according to Sachs, in a 400 mm. tube.

The estimation of the content of dry substance is made according to Claassen's method,⁵ the preliminary drying at a comparatively low temperature being dispensed with.

(b) In many factories, the extracted slices are dried, and an estimation of the sugar-content of the dried slices is required. In the case of normal products, very accurate results may be obtained fairly

¹ *Z. Ver. deut. Zuckerind.*, 1884, 34, 70.

³ *Z. Ver. deut. Zuckerind.*, 1909, 59, 627.

⁵ *Z. Ver. deut. Zuckerind.*, 1910, 60, 323.

² *Die Zuckerfabrikation*, p. 315.

⁴ *Sucrerie Belge*, 1909, 38, 147.

expeditiously by means of Herzfeld's modified method of alcoholic extraction,¹ which has also proved satisfactory for the examination of so-called "sugar slices" which contain a higher proportion of sugar.

According to this method, half the normal weight of the finely ground dry slices is digested in a 100 c.c. flask with 60 per cent. alcohol and 3-5 c.c. of basic lead acetate solution until the slices settle to the bottom, a process which takes twenty to thirty minutes. The digestion liquid is then rinsed into the extraction apparatus and extracted in the usual way; this requires, at most, from five to six hours. Should, as sometimes happens, part of the sucrose be inverted or caramelised, the total content of sucrose in the extract (after inversion) must be estimated gravimetrically.

The above-mentioned methods of Herzfeld and Sachs-Le Docte are better and more convenient. 50 g. of the sample are placed in a tared dish together with 125 c.c. of water, and left to steep for half an hour. Of the steeped, homogeneous mass, 60 g. in the case of dry slices, or 59 g. in the case of sugar slices, are weighed out and digested with 177 c.c. of diluted (150 c.c. to 1 litre of water) basic lead acetate solution; the polarimetric reading is to be multiplied by 3.5. If the slices can be triturated in a dry state, they are finely ground to powder in a mortar; 12.6 g. of this powder are subjected to hot, aqueous digestion, with 177 c.c. of diluted basic lead acetate solution (100 c.c. to 1 litre of water). The mixture is made up to 200 c.c., and the polarimeter reading is multiplied by 4.

4. PRESS MUD, DEFECATION MUD.

It is very difficult to get a representative sample from the press (even with Mehrle's sampling iron), and according to Claassen² this is best obtained in those factories in which it is the custom to macerate the mud to a pulp with a little water. If the analysis is to be made the basis of calculations of loss, the weight of the mud is best determined from the weight of lime employed (by multiplying by 3.5 or 4 for dry or wet mud respectively). In any case it is advisable to take the samples from the mud in the state in which it leaves the factory; all samples must be kept in closed vessels and thoroughly mixed prior to analysis.

The sucrose may be present, partly in the free state and partly combined with lime. According to Le Docte,³ the free sugar is determined as follows:—53 g. of the mud are treated with 177 c.c. of water (containing 2-3 c.c. of basic lead acetate solution), the whole is stirred and thoroughly mixed, best with a glass rod with a flattened

¹ *Z. Ver. deut. Zuckerind.*, 1909, 59, 627.

² *Die Zuckerfabrikation*, p. 316.

³ *Sucrierie Belge*, 1910, 38, 568.

end, and the rotation of the filtrate determined in a 400 mm. tube, the reading being divided by 2. For the estimation of the total sugar, Le Docte recommends the following form of the method originally described by Stammer and subsequently modified by Sidersky¹:—53 g. of the mud are treated with about half the quantity of 177 c.c. of pure water contained in a burette; the whole is stirred and mixed with a glass rod with a flattened end, and neutralised with concentrated acetic acid (of which about 3.7 c.c. are required); 3 c.c. of basic lead acetate solution are added, and then the remainder of the 177 c.c. of water, less 3.7+3 c.c. The whole is thoroughly stirred, filtered, and the rotation determined in a 400 mm. tube, the reading being divided by 2.

The method of Ost² and of Herles,³ in which solid ammonium nitrate or lead acetate is used for decomposing the mud, may be carried out in a similar way. The following method, which involves the use of ammonium nitrate, is quite as simple and trustworthy, and has the advantage that it permits of the simultaneous estimation of the sucrose as well as of the alkalinity of the mud. This method was worked out by Herzfeld⁴ in conformity with a proposal of Heyer:—53 g. of the cold mud are triturated, with gradual addition of 177 c.c. of a 10 per cent. solution of neutral ammonium nitrate, to a perfectly homogeneous mixture. The whole is filtered (no basic lead acetate solution being added!), and the rotation of the filtrate determined in a 200 mm. tube, the reading representing the percentage of sucrose. 10 c.c. of the filtrate are then titrated, in presence of rosolic acid, with standard acid of which 1 c.c. corresponds to 0.01 g. of calcium oxide. The number of cubic centimetres of acid required, multiplied by 0.38, gives the percentage of lime, CaO, in the mud.

III. THICK JUICES, SYRUPS.

A.—DETERMINATION OF SPECIFIC GRAVITY.

The determination of the specific gravity of thick juices and syrups is effected with the pycnometer or saccharometer. The relations between the specific gravity, degrees Balling (Brix) and Baumé are given in Table 46, p. 571. Concerning the estimation of water and of dry substance (from which the specific gravity can also be found) by means of the refractometer, see below (III., C, p. 600).

¹ *Bull. Assoc. Chim. Sucr.*, 1884, 2, 314.

³ *Z. Zuckerind. Böhm.*, 1908, 33, 1.

² *Z. Ver. deut. Zuckerind.*, 1882, 32, 659.

⁴ *Deutsche Zuckerindustrie*, 1909, 34, 973.

B.—ESTIMATION OF SUCROSE.

The cupric reduction methods of estimation in their application to products which contain only sucrose or only sucrose and invert sugar have been fully described above.

In cases where only the determination of the "polarisation" is required, this is carried out exactly as described under II., B. 1 (p. 578); alkaline juices are neutralised with a few drops of acetic acid prior to the addition of basic lead acetate solution (1-2 c.c.).

In the case of these intermediate products, however, the degree of rotation observed, as previously stated, does not always correspond to the actual content of sucrose; in many cases it is necessary to consider the presence of other optically active compounds. In practical beetroot sugar manufacture the most important of these compounds are invert sugar and raffinose; the former lowers the polarisation reading, the latter raises it. For the control of the value obtained by direct polarisation, the method, suggested by Clerget¹ and modified by Herzfeld,² of double observation, before and after inversion, may be used. The values found by this method for the original content of sucrose are quite exact if the invert sugar remains unchanged (*i.e.*, does not become partially decomposed by overheating) or if raffinose is actually present and not a mixture of other optically similar substances (see below). If the following working conditions³ are carefully observed, uniform and accurate results may be obtained; the slightest deviations, however, may cause serious errors.

Half the normal weight, *i.e.* 13 g. of the substance, is dissolved in 75 c.c. of water in a 100 c.c. flask, and treated with 5 c.c. of hydrochloric acid of sp. gr. 1.188 (*i.e.*, of 38 per cent. and containing 2.26 g. of hydrogen chloride). An accurate (standardised) thermometer is inserted in the flask and the latter is placed in the centre of a water-bath maintained at a uniform and constant temperature of 70°. By immersing the flask to a sufficient depth in the bath and keeping it constantly shaken it is heated to 67° in two to three minutes, and it is maintained at 67°-70° for exactly five minutes. The flask is then cooled at once to 20°, the thermometer withdrawn, the solution adhering thereto being rinsed into the flask, and the latter filled to the mark. If the solution is dark in colour, it is now decolorised by addition of 1-2 g. of bone charcoal, previously thoroughly extracted with hydrochloric acid and ignited (the absorptive power of the charcoal for invert sugar must be determined experimentally with a solution of pure invert sugar). The solution is then well shaken and filtered; if it is found to be insufficiently decolorised the first runnings of the

¹ *Ann. Chim. Phys.*, 1849 (3), 26, 201.

² *Z. Ver. deut. Zuckerind.*, 1890, 40, 165.

³ *Z. Ver. deut. Zuckerind.*, 1890, 40, 452.

filtrate are repeatedly returned to the filter. The filtrate is then poured into a 200 mm. water-jacketed tube, a thermometer, standardised and graduated to tenths of a degree, is inserted in the tube, and a current of water, at or near 20°, is passed through the jacket. As soon as the thermometer indicates a constant temperature, it is removed, and the rotation of the solution determined at once. The following formulæ¹ are used in calculating the result :—

Sucrose according to the improved formula of Clerget:—

$$S (\text{Sucrose}) = \frac{100K}{132.66},$$

in cases where the inversion “polarisation” is determined exactly at 20°, or :—

$$S = \frac{100K}{142.66 - \frac{t}{2}},$$

in cases where the inversion “polarisation” is determined at a temperature other than 20°.² In the above formulæ K represents the difference in the rotation in degrees of the saccharometer of the direct and inversion “polarisation” calculated on the normal weight, and *t* the temperature at which the inversion “polarisation” was determined.

*Sucrose according to the Raffinose formula.*³ (Applicable only in the presence of raffinose, see below.)

$$S (\text{Sucrose}) = \frac{0.5124P - I_{20}}{0.839}$$

In this case P represents the direct polarisation and *I*₂₀ the inversion polarisation at 20°, both calculated on the normal weight; if the inversion polarisation is taken at a temperature other than 20°, the observed value is corrected by Hammerschmidt's formula⁴ :—

$$I_{20} = I_t + 0.0038K(20 - t)$$

the value thus obtained being used in the first formula.

Table 50 contains all the numerical data necessary for the above optical inversion methods.

¹ For the deduction of these formulæ, cf. Herzfeld, *Z. Ver. deut. Zuckerind.*, 1890, 40, 165.

² After complete conversion into invert sugar, a sucrose solution of 100° dextro-rotation shows a lævo-rotation of 42°·66 at 0°; with rising temperature, this lævo-rotation falls by about 0°·5 for each degree Centigrade.

³ Cf. Creydt, *Z. Ver. deut. Zuckerind.*, 1887, 37, 153; Herzfeld and Dammüller, *ibid.*, 1888, 38, 742; Herzfeld, *ibid.*, 1890, 40, 194.

⁴ *Z. Ver. deut. Zuckerind.*, 1890, 40, 200.

Table 50.

Table for the Calculation of the Inversion Polarisation.

A. Temperature Corrections according to Hammerschmidt.

$I_{20} = I_t + 0.0038K(20 - t).$

K =	134.	132.	130.	128.	126.	124.	122.	120.	118.	116.	114.	112.	110.	105.	100.	95.	90.
20 - t = 1	0.51	0.50	0.49	0.49	0.48	0.47	0.46	0.46	0.45	0.44	0.43	0.43	0.42	0.40	0.38	0.36	0.34
2	1.02	1.00	0.99	0.97	0.96	0.94	0.93	0.91	0.90	0.88	0.87	0.85	0.84	0.80	0.76	0.72	0.68
3	1.53	1.50	1.48	1.46	1.44	1.41	1.39	1.37	1.35	1.32	1.30	1.28	1.25	1.20	1.14	1.08	1.03
4	2.04	2.01	1.98	1.95	1.92	1.88	1.85	1.82	1.79	1.76	1.73	1.70	1.67	1.60	1.52	1.44	1.37
5	2.55	2.51	2.47	2.43	2.39	2.36	2.32	2.28	2.24	2.20	2.17	2.13	2.09	2.00	1.90	1.81	1.71
6	3.06	3.01	2.96	2.92	2.87	2.83	2.78	2.74	2.69	2.64	2.60	2.55	2.51	2.39	2.28	2.17	2.05
7	3.56	3.51	3.46	3.40	3.35	3.30	3.25	3.19	3.14	3.09	3.03	2.98	2.93	2.79	2.66	2.53	2.39
8	4.07	4.01	3.95	3.89	3.83	3.77	3.71	3.65	3.59	3.53	3.47	3.40	3.34	3.19	3.04	2.89	2.74
9	4.58	4.51	4.45	4.38	4.31	4.24	4.17	4.10	4.04	3.97	3.90	3.83	3.76	3.59	3.42	3.25	3.08

K =	85.	80.	75.	70.	65.	60.	55.	50.	45.	40.	35.	30.	25.	20.	15.	10.	5.
20 - t = 1	0.32	0.30	0.29	0.27	0.25	0.23	0.21	0.19	0.17	0.15	0.13	0.11	0.10	0.08	0.06	0.04	0.02
2	0.65	0.61	0.57	0.53	0.49	0.46	0.42	0.38	0.34	0.30	0.27	0.23	0.19	0.15	0.11	0.08	0.04
3	0.97	0.91	0.86	0.80	0.74	0.68	0.63	0.57	0.51	0.46	0.40	0.34	0.29	0.23	0.17	0.11	0.06
4	1.29	1.22	1.14	1.06	0.99	0.91	0.84	0.76	0.68	0.61	0.53	0.46	0.38	0.30	0.23	0.15	0.08
5	1.62	1.52	1.43	1.33	1.24	1.14	1.05	0.95	0.86	0.76	0.67	0.57	0.48	0.38	0.29	0.19	0.10
6	1.94	1.82	1.71	1.60	1.48	1.37	1.25	1.14	1.03	0.91	0.80	0.68	0.57	0.46	0.34	0.23	0.11
7	2.26	2.13	2.00	1.86	1.73	1.60	1.46	1.33	1.20	1.06	0.93	0.80	0.67	0.53	0.40	0.27	0.13
8	2.58	2.43	2.28	2.13	1.98	1.82	1.67	1.52	1.37	1.22	1.06	0.91	0.76	0.61	0.46	0.30	0.15
9	2.91	2.74	2.57	2.39	2.22	2.05	1.88	1.71	1.54	1.37	1.20	1.03	0.86	0.68	0.51	0.34	0.17

B. Sucrose according to Clerget.

$S = \frac{100K}{132.66} = 0.75880K.$ 0.75380.					
1	0.7538	6	4.5228	10	7.5380
2	1.5076	7	5.2766	11	8.2918
3	2.2614	8	6.0304	12	9.0456
4	3.0152	9	6.7842	13	9.7994
5	3.7690				

C. Sucrose and Raffinose according to the Formulae.

$S = \frac{0.5188P - I_{20}}{0.845}$ $= 0.61396P - 1.18343I_{20}$ $0.61396 \qquad 1.18343.$				$R = \frac{P-S}{1.85}$ $= 0.5405 (P-Z)$ $0.5405.$		$S = \frac{0.5124P - I_{20}}{0.839}$ $= 0.61073P - 1.19190I_{20}$ $0.61073 \qquad 1.19190.$			
1	0.6140	1	1.1834	1	0.541	1	0.6107	1	1.1919
2	1.2279	2	2.3669	2	1.081	2	1.2215	2	2.3838
3	1.8419	3	3.5503	3	1.622	3	1.8322	3	3.5757
4	2.4558	4	4.7337	4	2.162	4	2.4429	4	4.7676
5	3.0698	5	5.9172	5	2.703	5	3.0537	5	5.9595
6	3.6838	6	7.1006	6	3.243	6	3.6644	6	7.1514
7	4.2977	7	8.2840	7	3.784	7	4.2751	7	8.3433
8	4.9117	8	9.4674	8	4.324	8	4.8858	8	9.5352
9	5.5256	9	10.6509	9	4.865	9	5.4966	9	10.7271
10	6.1396	10	11.8343	10	5.405	10	6.1073	10	11.9190

For the control of the optical method it is useful in many cases¹ to estimate the total amount of sucrose in the inverted solution by means of Fehling's solution. For this purpose, 50 c.c. of the solution used for polarisation are made up to 1 litre, and 25 c.c. of the diluted solution (containing 0.1625 g. of substance) are neutralised with 25 c.c. of a solution containing 1.7 g. of anhydrous sodium carbonate per litre. The neutralised solution is then treated as described on p. 561.

C.—ESTIMATION OF WATER AND OF NON-SUGAR CONSTITUENTS.

The direct estimation of the content of dry substance is effected by weighing out 3 g. of the material together with 50 g. of sand, and drying *in vacuo* at 105°–110°.

The content of water can be estimated very simply and quickly by the recently much-improved refractometric method; using the Abbé refractometer, only 2–3 drops of the sugar solution under examination are required for the estimation. The liquid is placed between the two prisms of the instrument and the determination is carried out in conformity with the details of the method supplied with each apparatus. By causing a current of water (adjusted to a temperature of 20° by means of an accurate thermometer) to flow in contact with the prisms, the small quantity of sugar solution may quickly be brought to the normal temperature of 20°, the refractive index then being read at once.

¹ Cf. Lippmann, *Chemie der Zuckerarten*, p. 1659; Baumann, *Z. Ver. deut. Zuckerind.*, 1898, 48, 780.

The corresponding content of water or of dry substance is then found directly from the Table compiled by Main¹ (Table 51, p. 602). If it is not practicable to adjust the temperature to 20°, the temperature of the water in contact with the prisms is determined at each reading, the refractive index then being corrected by means of a Table compiled by Stanek² (Table 52, p. 606).

Main's Table has recently been checked by Schönrock, working in the laboratories of the *Physikalisch-Technische Reichsanstalt*, Berlin. His results show no greater deviation from those of Main than 4 in the fourth place of decimals.

In the case of pure sugar juices, the results agree practically exactly with the actual values; in the case of impure solutions the results are not nearly so much affected by the presence of non-sugar substances as the results obtained with either Brix's hydrometer or Mohr's balance, and they are therefore sufficiently accurate for all practical purposes.

¹ *Int. Sugar J.*, 1907, 9, 481.

² *Z. Zuckerind. Böhm.*, 1908, 33, 153; for a Table of corrections for the so-called Immersion Refractometer, cf. *ibid.*, 1910, 34, 501.

Table 51.

Table for estimating the Water-Content of Sugar Solutions by means of the Abbé Refractometer. (Main.)

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1.3330	100.0	1.3408	94.5	1.3491	89.0	1.3579	83.5
1.3331	99.9	1.3409	94.4	1.3492	88.9	1.3581	83.4
1.3333	99.8	1.3411	94.3	1.3494	88.8	1.3582	83.3
1.3334	99.7	1.3412	94.2	1.3496	88.7	1.3584	83.2
1.3336	99.6	1.3414	94.1	1.3497	88.6	1.3586	83.1
1.3337	99.5	1.3415	94.0	1.3499	88.5	1.3587	83.0
1.3338	99.4	1.3417	93.9	1.3500	88.4	1.3589	82.9
1.3340	99.3	1.3418	93.8	1.3502	88.3	1.3591	82.8
1.3341	99.2	1.3420	93.7	1.3503	88.2	1.3592	82.7
1.3343	99.1	1.3421	93.6	1.3505	88.1	1.3594	82.6
1.3344	99.0	1.3423	93.5	1.3507	88.0	1.3596	82.5
1.3345	98.9	1.3424	93.4	1.3508	87.9	1.3597	82.4
1.3347	98.8	1.3426	93.3	1.3510	87.8	1.3599	82.3
1.3348	98.7	1.3427	93.2	1.3511	87.7	1.3600	82.2
1.3350	98.6	1.3429	93.1	1.3513	87.6	1.3602	82.1
1.3351	98.5	1.3430	93.0	1.3515	87.5	1.3604	82.0
1.3352	98.4	1.3432	92.9	1.3516	87.4	1.3605	81.9
1.3354	98.3	1.3433	92.8	1.3518	87.3	1.3607	81.8
1.3355	98.2	1.3435	92.7	1.3519	87.2	1.3609	81.7
1.3357	98.1	1.3436	92.6	1.3521	87.1	1.3610	81.6
1.3358	98.0	1.3438	92.5	1.3522	87.0	1.3612	81.5
1.3359	97.9	1.3439	92.4	1.3524	86.9	1.3614	81.4
1.3361	97.8	1.3441	92.3	1.3526	86.8	1.3615	81.3
1.3362	97.7	1.3442	92.2	1.3527	86.7	1.3617	81.2
1.3364	97.6	1.3444	92.1	1.3529	86.6	1.3619	81.1
1.3365	97.5	1.3445	92.0	1.3530	86.5	1.3620	81.0
1.3366	97.4	1.3447	91.9	1.3532	86.4	1.3622	80.9
1.3368	97.3	1.3448	91.8	1.3533	86.3	1.3624	80.8
1.3369	97.2	1.3450	91.7	1.3535	86.2	1.3625	80.7
1.3371	97.1	1.3451	91.6	1.3537	86.1	1.3627	80.6
1.3372	97.0	1.3453	91.5	1.3538	86.0	1.3629	80.5
1.3373	96.9	1.3454	91.4	1.3540	85.9	1.3630	80.4
1.3375	96.8	1.3456	91.3	1.3541	85.8	1.3632	80.3
1.3376	96.7	1.3457	91.2	1.3543	85.7	1.3634	80.2
1.3378	96.6	1.3459	91.1	1.3545	85.6	1.3635	80.1
1.3379	96.5	1.3460	91.0	1.3546	85.5	1.3637	80.0
1.3380	96.4	1.3462	90.9	1.3548	85.4	1.3639	79.9
1.3382	96.3	1.3463	90.8	1.3549	85.3	1.3640	79.8
1.3383	96.2	1.3465	90.7	1.3551	85.2	1.3642	79.7
1.3385	96.1	1.3466	90.6	1.3552	85.1	1.3644	79.6
1.3386	96.0	1.3468	90.5	1.3554	85.0	1.3645	79.5
1.3387	95.9	1.3469	90.4	1.3556	84.9	1.3647	79.4
1.3389	95.8	1.3471	90.3	1.3557	84.8	1.3649	79.3
1.3390	95.7	1.3472	90.2	1.3559	84.7	1.3650	79.2
1.3392	95.6	1.3474	90.1	1.3561	84.6	1.3652	79.1
1.3393	95.5	1.3475	90.0	1.3562	84.5	1.3654	79.0
1.3394	95.4	1.3477	89.9	1.3564	84.4	1.3655	78.9
1.3396	95.3	1.3478	89.8	1.3566	84.3	1.3657	78.8
1.3397	95.2	1.3480	89.7	1.3567	84.2	1.3659	78.7
1.3399	95.1	1.3481	89.6	1.3569	84.1	1.3661	78.6
1.3400	95.0	1.3483	89.5	1.3571	84.0	1.3662	78.5
1.3402	94.9	1.3484	89.4	1.3572	83.9	1.3664	78.4
1.3403	94.8	1.3486	89.3	1.3574	83.8	1.3666	78.3
1.3405	94.7	1.3488	89.2	1.3576	83.7	1.3667	78.2
1.3406	94.6	1.3489	89.1	1.3577	83.6	1.3669	78.1

Table 51—continued.

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1.3671	78.0	1.3773	72.1	1.3880	66.2	1.3991	60.3
1.3672	77.9	1.3774	72.0	1.3882	66.1	1.3993	60.2
1.3674	77.8	1.3776	71.9	1.3884	66.0	1.3995	60.1
1.3676	77.7	1.3778	71.8	1.3885	65.9	1.3997	60.0
1.3677	77.6	1.3780	71.7	1.3887	65.8	1.3999	59.9
1.3679	77.5	1.3782	71.6	1.3889	65.7	1.4001	59.8
1.3681	77.4	1.3783	71.5	1.3891	65.6	1.4003	59.7
1.3682	77.3	1.3785	71.4	1.3893	65.5	1.4005	59.6
1.3684	77.2	1.3787	71.3	1.3895	65.4	1.4007	59.5
1.3686	77.1	1.3789	71.2	1.3896	65.3	1.4009	59.4
1.3687	77.0	1.3790	71.1	1.3898	65.2	1.4011	59.3
1.3689	76.9	1.3792	71.0	1.3900	65.1	1.4013	59.2
1.3691	76.8	1.3794	70.9	1.3902	65.0	1.4015	59.1
1.3692	76.7	1.3796	70.8	1.3904	64.9	1.4017	59.0
1.3694	76.6	1.3798	70.7	1.3906	64.8	1.4019	58.9
1.3696	76.5	1.3799	70.6	1.3908	64.7	1.4021	58.8
1.3697	76.4	1.3801	70.5	1.3910	64.6	1.4022	58.7
1.3699	76.3	1.3803	70.4	1.3912	64.5	1.4024	58.6
1.3701	76.2	1.3805	70.3	1.3913	64.4	1.4026	58.5
1.3703	76.1	1.3806	70.2	1.3915	64.3	1.4028	58.4
1.3704	76.0	1.3808	70.1	1.3917	64.2	1.4030	58.3
1.3706	75.9	1.3810	70.0	1.3919	64.1	1.4032	58.2
1.3708	75.8	1.3812	69.9	1.3921	64.0	1.4034	58.1
1.3709	75.7	1.3814	69.8	1.3923	63.9	1.4036	58.0
1.3711	75.6	1.3816	69.7	1.3925	63.8	1.4038	57.9
1.3713	75.5	1.3817	69.6	1.3927	63.7	1.4040	57.8
1.3714	75.4	1.3819	69.5	1.3929	63.6	1.4042	57.7
1.3716	75.3	1.3821	69.4	1.3931	63.5	1.4044	57.6
1.3718	75.2	1.3823	69.3	1.3932	63.4	1.4046	57.5
1.3719	75.1	1.3825	69.2	1.3934	63.3	1.4048	57.4
1.3721	75.0	1.3827	69.1	1.3936	63.2	1.4050	57.3
1.3723	74.9	1.3828	69.0	1.3938	63.1	1.4052	57.2
1.3725	74.8	1.3830	68.9	1.3940	63.0	1.4054	57.1
1.3726	74.7	1.3832	68.8	1.3942	62.9	1.4056	57.0
1.3728	74.6	1.3834	68.7	1.3944	62.8	1.4058	56.9
1.3730	74.5	1.3836	68.6	1.3946	62.7	1.4060	56.8
1.3732	74.4	1.3838	68.5	1.3948	62.6	1.4062	56.7
1.3733	74.3	1.3839	68.4	1.3950	62.5	1.4064	56.6
1.3735	74.2	1.3841	68.3	1.3951	62.4	1.4066	56.5
1.3737	74.1	1.3843	68.2	1.3953	62.3	1.4068	56.4
1.3739	74.0	1.3845	68.1	1.3955	62.2	1.4070	56.3
1.3741	73.9	1.3847	68.0	1.3957	62.1	1.4071	56.2
1.3742	73.8	1.3849	67.9	1.3959	62.0	1.4073	56.1
1.3744	73.7	1.3850	67.8	1.3961	61.9	1.4075	56.0
1.3746	73.6	1.3852	67.7	1.3963	61.8	1.4077	55.9
1.3748	73.5	1.3854	67.6	1.3965	61.7	1.4079	55.8
1.3749	73.4	1.3856	67.5	1.3967	61.6	1.4081	55.7
1.3751	73.3	1.3858	67.4	1.3969	61.5	1.4083	55.6
1.3753	73.2	1.3860	67.3	1.3970	61.4	1.4085	55.5
1.3755	73.1	1.3862	67.2	1.3972	61.3	1.4087	55.4
1.3757	73.0	1.3863	67.1	1.3974	61.2	1.4089	55.3
1.3758	72.9	1.3865	67.0	1.3976	61.1	1.4091	55.2
1.3760	72.8	1.3867	66.9	1.3978	61.0	1.4093	55.1
1.3762	72.7	1.3869	66.8	1.3980	60.9	1.4095	55.0
1.3764	72.6	1.3871	66.7	1.3982	60.8	1.4097	54.9
1.3766	72.5	1.3873	66.6	1.3984	60.7	1.4099	54.8
1.3767	72.4	1.3874	66.5	1.3986	60.6	1.4101	54.7
1.3769	72.3	1.3876	66.4	1.3988	60.5	1.4103	54.6
1.3771	72.2	1.3878	66.3	1.3989	60.4	1.4106	54.5

Table 51—continued.

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1.4108	54.4	1.4232	48.5	1.4359	42.6	1.4496	36.7
1.4110	54.3	1.4234	48.4	1.4362	42.5	1.4498	36.6
1.4112	54.2	1.4236	48.3	1.4364	42.4	1.4500	36.5
1.4114	54.1	1.4238	48.2	1.4366	42.3	1.4503	36.4
1.4116	54.0	1.4240	48.1	1.4368	42.2	1.4505	36.3
1.4118	53.9	1.4242	48.0	1.4371	42.1	1.4507	36.2
1.4120	53.8	1.4244	47.9	1.4373	42.0	1.4509	36.1
1.4123	53.7	1.4246	47.8	1.4375	41.9	1.4512	36.0
1.4125	53.6	1.4248	47.7	1.4378	41.8	1.4514	35.9
1.4127	53.5	1.4250	47.6	1.4380	41.7	1.4516	35.8
1.4129	53.4	1.4253	47.5	1.4382	41.6	1.4519	35.7
1.4131	53.3	1.4255	47.4	1.4385	41.5	1.4521	35.6
1.4133	53.2	1.4257	47.3	1.4387	41.4	1.4523	35.5
1.4135	53.1	1.4259	47.2	1.4389	41.3	1.4526	35.4
1.4137	53.0	1.4261	47.1	1.4391	41.2	1.4528	35.3
1.4140	52.9	1.4263	47.0	1.4394	41.1	1.4530	35.2
1.4142	52.8	1.4265	46.9	1.4396	41.0	1.4533	35.1
1.4144	52.7	1.4267	46.8	1.4398	40.9	1.4535	35.0
1.4146	52.6	1.4269	46.7	1.4401	40.8	1.4537	34.9
1.4148	52.5	1.4271	46.6	1.4403	40.7	1.4540	34.8
1.4150	52.4	1.4273	46.5	1.4405	40.6	1.4542	34.7
1.4152	52.3	1.4275	46.4	1.4408	40.5	1.4544	34.6
1.4154	52.2	1.4277	46.3	1.4410	40.4	1.4547	34.5
1.4156	52.1	1.4279	46.2	1.4412	40.3	1.4549	34.4
1.4159	52.0	1.4281	46.1	1.4414	40.2	1.4551	34.3
1.4161	51.9	1.4283	46.0	1.4417	40.1	1.4554	34.2
1.4163	51.8	1.4285	45.9	1.4419	40.0	1.4556	34.1
1.4165	51.7	1.4288	45.8	1.4421	39.9	1.4558	34.0
1.4167	51.6	1.4290	45.7	1.4424	39.8	1.4561	33.9
1.4169	51.5	1.4292	45.6	1.4426	39.7	1.4563	33.8
1.4171	51.4	1.4294	45.5	1.4428	39.6	1.4565	33.7
1.4173	51.3	1.4296	45.4	1.4431	39.5	1.4567	33.6
1.4176	51.2	1.4298	45.3	1.4433	39.4	1.4570	33.5
1.4178	51.1	1.4300	45.2	1.4435	39.3	1.4572	33.4
1.4180	51.0	1.4302	45.1	1.4438	39.2	1.4574	33.3
1.4182	50.9	1.4304	45.0	1.4440	39.1	1.4577	33.2
1.4184	50.8	1.4306	44.9	1.4442	39.0	1.4579	33.1
1.4186	50.7	1.4309	44.8	1.4445	38.9	1.4581	33.0
1.4188	50.6	1.4311	44.7	1.4447	38.8	1.4584	32.9
1.4190	50.5	1.4313	44.6	1.4449	38.7	1.4586	32.8
1.4193	50.4	1.4316	44.5	1.4451	38.6	1.4588	32.7
1.4195	50.3	1.4318	44.4	1.4454	38.5	1.4591	32.6
1.4197	50.2	1.4320	44.3	1.4456	38.4	1.4593	32.5
1.4199	50.1	1.4322	44.2	1.4458	38.3	1.4595	32.4
1.4201	50.0	1.4325	44.1	1.4461	38.2	1.4598	32.3
1.4203	49.9	1.4327	44.0	1.4463	38.1	1.4600	32.2
1.4205	49.8	1.4329	43.9	1.4465	38.0	1.4602	32.1
1.4207	49.7	1.4332	43.8	1.4468	37.9	1.4605	32.0
1.4209	49.6	1.4334	43.7	1.4470	37.8	1.4607	31.9
1.4211	49.5	1.4336	43.6	1.4472	37.7	1.4609	31.8
1.4213	49.4	1.4339	43.5	1.4475	37.6	1.4612	31.7
1.4215	49.3	1.4341	43.4	1.4477	37.5	1.4614	31.6
1.4217	49.2	1.4343	43.3	1.4479	37.4	1.4616	31.5
1.4220	49.1	1.4345	43.2	1.4482	37.3	1.4619	31.4
1.4222	49.0	1.4348	43.1	1.4484	37.2	1.4621	31.3
1.4224	48.9	1.4350	43.0	1.4486	37.1	1.4623	31.2
1.4226	48.8	1.4352	42.9	1.4489	37.0	1.4625	31.1
1.4228	48.7	1.4355	42.8	1.4491	36.9	1.4628	31.0
1.4230	48.6	1.4357	42.7	1.4493	36.8	1.4630	30.9

Table 51—*continued.*

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1·4632	30·8	1·4730	26·8	1·4830	22·8	1·4933	18·8
1·4635	30·7	1·4732	26·7	1·4832	22·7	1·4935	18·7
1·4637	30·6	1·4735	26·6	1·4835	22·6	1·4938	18·6
1·4639	30·5	1·4737	26·5	1·4838	22·5	1·4941	18·5
1·4642	30·4	1·4740	26·4	1·4840	22·4	1·4943	18·4
1·4644	30·3	1·4742	26·3	1·4843	22·3	1·4946	18·3
1·4646	30·2	1·4744	26·2	1·4845	22·2	1·4949	18·2
1·4649	30·1	1·4747	26·1	1·4848	22·1	1·4951	18·1
1·4651	30·0	1·4749	26·0	1·4850	22·0	1·4954	18·0
1·4653	29·9	1·4752	25·9	1·4853	21·9	1·4956	17·9
1·4656	29·8	1·4754	25·8	1·4855	21·8	1·4959	17·8
1·4658	29·7	1·4757	25·7	1·4858	21·7	1·4962	17·7
1·4661	29·6	1·4759	25·6	1·4860	21·6	1·4964	17·6
1·4663	29·5	1·4762	25·5	1·4863	21·5	1·4967	17·5
1·4666	29·4	1·4764	25·4	1·4865	21·4	1·4970	17·4
1·4668	29·3	1·4767	25·3	1·4868	21·3	1·4972	17·3
1·4671	29·2	1·4769	25·2	1·4871	21·2	1·4975	17·2
1·4673	29·1	1·4772	25·1	1·4873	21·1	1·4978	17·1
1·4676	29·0	1·4774	25·0	1·4876	21·0	1·4980	17·0
1·4678	28·9	1·4777	24·9	1·4878	20·9	1·4983	16·9
1·4681	28·8	1·4779	24·8	1·4881	20·8	1·4985	16·8
1·4683	28·7	1·4782	24·7	1·4883	20·7	1·4988	16·7
1·4685	28·6	1·4784	24·6	1·4886	20·6	1·4991	16·6
1·4688	28·5	1·4787	24·5	1·4888	20·5	1·4993	16·5
1·4690	28·4	1·4789	24·4	1·4891	20·4	1·4996	16·4
1·4693	28·3	1·4792	24·3	1·4893	20·3	1·4999	16·3
1·4695	28·2	1·4794	24·2	1·4896	20·2	1·5001	16·2
1·4698	28·1	1·4797	24·1	1·4898	20·1	1·5004	16·1
1·4700	28·0	1·4799	24·0	1·4901	20·0	1·5007	16·0
1·4703	27·9	1·4802	23·9	1·4904	19·9	1·5009	15·9
1·4705	27·8	1·4804	23·8	1·4906	19·8	1·5012	15·8
1·4708	27·7	1·4807	23·7	1·4909	19·7	1·5015	15·7
1·4710	27·6	1·4810	23·6	1·4912	19·6	1·5017	15·6
1·4713	27·5	1·4812	23·5	1·4914	19·5	1·5020	15·5
1·4715	27·4	1·4815	23·4	1·4917	19·4	1·5022	15·4
1·4717	27·3	1·4817	23·3	1·4919	19·3	1·5025	15·3
1·4720	27·2	1·4820	23·2	1·4922	19·2	1·5028	15·2
1·4722	27·1	1·4822	23·1	1·4925	19·1	1·5030	15·1
1·4725	27·0	1·4825	23·0	1·4927	19·0	1·5033	15·0
1·4727	26·9	1·4827	22·9	1·4930	18·9		

Table 52.

Table of Corrections for the Percentages of Water found below and above 20°, by means of the Abbé Refractometer. (Stanek.)

Temperature °C.	Percentage of water.									
	95.	90.	85.	80.	70.	60.	50.	40.	30.	25.
Add to the percentage of water.										
15	0·25	0·27	0·31	0·31	0·34	0·35	0·36	0·37	0·36	0·36
16	0·21	0·23	0·26	0·27	0·29	0·31	0·31	0·32	0·31	0·29
17	0·16	0·18	0·20	0·20	0·22	0·23	0·23	0·23	0·20	0·17
18	0·11	0·12	0·14	0·14	0·15	0·16	0·16	0·15	0·12	0·09
19	0·06	0·07	0·08	0·08	0·08	0·09	0·09	0·08	0·07	0·05
Subtract from the percentage of water.										
21	0·06	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07
22	0·12	0·14	0·14	0·14	0·14	0·14	0·15	0·14	0·14	0·14
23	0·18	0·20	0·20	0·21	0·21	0·21	0·23	0·21	0·22	0·22
24	0·24	0·26	0·26	0·27	0·28	0·28	0·30	0·28	0·29	0·29
25	0·30	0·32	0·32	0·34	0·36	0·36	0·38	0·36	0·36	0·37
26	0·36	0·39	0·39	0·41	0·43	0·43	0·46	0·44	0·43	0·44
27	0·43	0·46	0·46	0·48	0·50	0·51	0·55	0·62	0·50	0·51
28	0·50	0·53	0·53	0·55	0·58	0·59	0·63	0·70	0·57	0·59
29	0·57	0·60	0·61	0·62	0·66	0·67	0·71	0·78	0·65	0·67
30	0·64	0·67	0·70	0·71	0·74	0·75	0·80	0·86	0·73	0·75

Examples :

1.

Water-content as found at 15° .

.

.

90·00 per cent.
- Temperature correction

.

.

+0·27

”
- Corrected water-content

.

.

90·27

”
2.

Water-content as found at 17°·5

.

.

90·00

”
- Temperature correction

.

.

+0·15

”
- (The mean between 0·12 and 0·18.)

D.—ESTIMATION OF ASH.

This is carried out with 2-3 g. of the juice according to the method described in II., *D* (p. 589).

E.—ESTIMATION OF INVERT SUGAR.

With small quantities the method given under I., *C, a* (p. 555), is used ; with larger quantities, that given under I., *C, b* (p. 558), or I., *C, c* (p. 561), is employed. The method described on p. 564 may also be used.

F.—ESTIMATION OF RAFFINOSE (ALSO IN PRESENCE OF
INVERT SUGAR).

Since raffinose is present in the beetroot, its occurrence in all the products of beetroot sugar manufacture is possible. Owing to the great solubility of this sugar, however, large quantities are only found in the final products and molasses and chiefly in the sugar obtained by the de-saccharification of molasses. For the analysis of such products the raffinose formula has been worked out; its use is confined chiefly to those products which, owing to their origin, certainly, or at least very probably, contain raffinose. If substances of different origin are analysed according to this formula, serious errors may be introduced, since many non-sugar substances, especially certain products of the overheating and decomposition of sugar, show an optical behaviour analogous to that of raffinose, and thus may give an indication of raffinose when none of the latter is present. Moreover, in cases where such substances accompany raffinose, the raffinose formula is of course uncertain and inapplicable.

The optical estimation of raffinose is carried out by Herzfeld's method, and in addition to the value S for sucrose the Table C (p. 600) gives the value for anhydrous raffinose, $S = \frac{P-S}{1.852}$. Besides the Clerget-

Herzfeld method of optical inversion, Scheibler's extraction method¹ (by means of methyl alcohol saturated with sugar) and Creydt's mucic acid method² have been proposed for the quantitative estimation of raffinose in the presence of sucrose. Neither of these methods has, however, been introduced into practice; the first has not been sufficiently worked out, while the second requires too much time (three days), and although with mixtures of pure sucrose and pure raffinose it gives results agreeing to within a few tenths per cent., in the case of commercial sugars, syrups, or molasses, serious differences are introduced. For instance, the presence of other substances which also yield mucic acid on oxidation causes the amount of the latter to appear much too high; on the other hand, from very impure solutions containing much organic matter the mucic acid often does not separate completely.

If it is desired to determine whether a substance, which according to its optical behaviour appears to be raffinose, actually is this compound, the mucic acid method may serve as a very valuable control; a special

¹ *Ber.*, 1885, 18, 1409.

² *Z. Ver. deut. Zuckerind.*, 1887, 37, 153; cf. also Lippmann, *Chemie der Zuckerarten*, p. 1652.

method, useful for the rapid detection of raffinose, has also been worked out by Ofner.¹

Only those products can be examined according to the raffinose formula which contain raffinose and sucrose only, or at the most such small quantities of invert sugar in addition as to be negligible in calculation. For cases in which larger quantities of invert sugar occur, Wortmann² has worked out a method by means of which the three constituents may be determined from the direct "polarisation," the inversion "polarisation," and the invert sugar-content as found directly by the Meissel-Hiller method (*cf.* I., C, b, p. 558). According to Baumann,³ however, with a high content of invert sugar the direct "polarisation" is too uncertain a factor for calculation, and therefore the following method is preferable:—The total sugar is estimated in the inverted solution (see p. 555) with Fehling's solution according to Herzfeld's methods (with 0.1625 g. of substance); the copper thus reduced is produced by—(1) the invert sugar originally present and that formed from the sucrose by inversion; (2) the reducing action of the inversion products of the raffinose. In addition to this determination the inversion "polarisation" is found (according to the methods described above). The following formulæ are used for calculation:—

$$\text{I. } S = \frac{582.98 \times C - (I \times F^2)}{0.9491 \times F^1 + 0.3266 \times F^2}$$

$$\text{II. } R = 1.054 \times I + 0.344 \times S$$

In these formulæ—

S represents the content of sucrose + invert sugar, the latter calculated as sucrose (total sugar).

R the content of anhydrous raffinose.

C the total quantity of copper precipitated.

I the inversion polarisation.

F¹ the reduction factor of inverted sucrose.

F² the reduction factor of inverted raffinose.

The reduction factors, F¹ and F², are obtained by taking the numbers found for copper from the Tables for the calculation of the content of sucrose⁴ and raffinose⁵ respectively, and dividing them by the corresponding numbers for sucrose and raffinose. Since, however, the reduction factors only fall slowly they need not be calculated for each case; it is sufficient to do this for each 10 mg. Cu. For the quantities of copper generally obtained in practice, from

¹ *Z. Zuckerind. Böhm.*, 1907, 31, 326.

² *Z. Ver. deut. Zuckerind.*, 1888, 38, 714; 1890, 40, 786.

⁴ *Ibid.*, 1888, 38, 714; 1890, 40, 786.

³ *Ibid.*, 1888, 38, 741.

⁵ *Ibid.*, 1888, 38, 741.

0.150-0.200 g., the following simplified formula of Baumann may be used:—

$$\begin{array}{l}
 C = \\
 \begin{array}{l}
 0.150 \\
 0.160 \\
 0.170 \\
 0.180 \\
 0.190 \\
 0.200
 \end{array}
 \left\{ \begin{array}{l}
 248.1 \times C - 0.605 \times I \\
 248.4 \times C - 0.604 \times I \\
 248.7 \times C - 0.604 \times I \\
 249.2 \times C - 0.604 \times I \\
 249.7 \times C - 0.604 \times I \\
 250.0 \times C - 0.604 \times I
 \end{array} \right\} R = 1.054 \times 0.344 S.
 \end{array}$$

If, in addition to the total sugar, it is desired to estimate the sucrose present as such, a direct estimation of invert sugar is made by the method of Meissel-Hiller (p. 558), for which the total sugar-content, determined according to the above formulæ, is used for calculating Hiller's factor, F , instead of the direct polarisation. From the content of invert sugar found, one-twentieth is deducted; by subtracting the remainder (which represents the amount of sucrose equivalent to the amount of invert sugar present) from the total sugar-content the content of sucrose present in the sample is found.

The following example will serve to illustrate the use of the above formulæ:—

The following values were obtained in the analysis of a syrup:—

1. Inversion "polarisation": $I = -8^\circ.5$.
2. Copper obtained after inversion from 0.1625 g. of substance: $Cu = 0.184$ g.
3. Copper obtained before inversion (direct estimation of invert sugar) from 2.0 g. of substance: $Cu_1 = 0.250$ g.

For the general formula for total sugar the factors $F^1 = \frac{184}{93.1}$ and $F^2 = \frac{183.6}{130}$ must be taken from the corresponding Tables; the above simplified formula for $C = 0.180$ may be used, however. Accordingly:—

$$S = 249.2 \times 0.184 - 0.604 \times (-8.5) = 50.98$$

$$R = 1.054 \times (-8.5) + 0.344 \times 50.98 = 8.58$$

In order to determine the proportion of sucrose (S) to invert sugar (I) using Hiller's formula:—

$$I = \frac{\frac{100C_1}{2}}{p} = 6.25$$

$$\text{Therefore:—} S + I : I = 50.98 : 6.25 = 100 : 12$$

$$\text{and } S : I = 88 : 12$$

$$I = \frac{0.250 \times 52.6}{2} = 6.58$$

For the conversion of invert sugar into sucrose $\frac{1}{20}$ is subtracted from the value for I, and consequently 6.25 subtracted from the total sugar.

$$S = 50.98 - 6.25 = 44.73$$

Hence the sample of syrup contains:—

44.73	per cent.	sucrose
6.58	„	invert sugar
8.58	„	raffinose

G.—ESTIMATION OF COLOUR.

See under II., G (p. 592).

H.—ESTIMATION OF ALKALINITY.

For this estimation 10 c.c. of the juice are diluted with distilled water previously neutralised, and titrated with $N/28$ acid, phenolphthalein being used as indicator. Cf. II., F (p. 591).

The amount of lime is determined in 5.15 g. of the juice (according to the quantity present) by the method described on p. 592.

IV. MASSECUITES.

A.—ESTIMATION OF DRY SUBSTANCE AND OF SPECIFIC GRAVITY.

An accurate estimation of the dry substance or of the specific gravity can only be made by drying the material, and this is indispensable if the content of dry substance (or the corresponding degrees Brix) is to serve as a basis for calculating the purity, since with massecuites the apparent and true purities often differ very considerably, and not always in the same direction. For the estimation, 2-3 g. of the massecuite is thoroughly mixed with sand (50 g.), the mixture dried for fifteen minutes at 70° , again mixed, and then dried for six to eight hours at 105° - 110° , in an air-oven or *in vacuo*. On further drying for two hours the weight should not diminish by more than 0.1 per cent. at most.

Sachs¹ employs the following method:—78 g. (*i.e.* thrice the normal weight) of the perfectly homogeneous massecuite are dissolved in 300 c.c. of water. 10 c.c. of this solution are stirred with 12-15 g. of sand in a small dish, the mixture being dried first at 100° , and then with the temperature rising slowly to 107° , until, after some hours, constant weight is attained. If a massecuite shows an acid reaction, as is sometimes the case, it must be neutralised with a sodium carbonate solution of known concentration, the amount of dry

¹ *Sucrerie Belge*, 1901, 29, 313; *Oesterr.-Ungar. Zeitschr.* 1901, p. 366.

substance thus added being allowed for; according to Pellet¹ ammonia may be used with advantage for neutralisation instead of sodium carbonate.

Accurate results, approximating closely to those obtained by drying the massecuite, can be obtained by means of the Abbé refractometer. For this purpose, the massecuite is dissolved in a known quantity of water (preferably in an equal weight of water), and the solution examined as described under III., *A*; in making the calculation the quantity of water added must of course be taken into account.

If only an approximately accurate estimation of the specific gravity of a massecuite is required (as is often the case in practice), a pykno-metric method, originally suggested for molasses by Sidersky,² is generally used. The massecuite is warmed on the water-bath until it is mobile, and is then transferred to a dry, weighed, and previously warmed graduated flask (a 50 c.c. flask, the neck of which has been cut off above the mark). The flask is filled to a little below the mark, cooled to the normal temperature (20°), and weighed. The flask is then filled very carefully, so that no mixing occurs, to the mark with water at 20°. If n cubic centimetres of water have been added, $50-n$ is the volume of the massecuite taken, and since its weight has also been determined, its specific gravity may be found at once. It is evident that the accuracy of the result depends on the homogeneity of the massecuite, and especially on the absence of air-bubbles; this is extremely difficult to ensure with certainty, so that the limit of error with this much used method is a wide one, especially in the case of massecuite that has been boiled to grain.

For merely comparative determinations (*e.g.*, for purposes of daily control) it is sufficient to take the hydrometer reading of a solution of 26 g. of massecuite made up to 100 c.c. or to dissolve a larger quantity (*e.g.* 200 g.) of the massecuite in warm water in a tared beaker, and, after cooling to the normal temperature, to dilute it to double the weight (400 g.) with water, the degrees Brix of this solution then being determined; the result is multiplied by 2, and the specific gravity found from Table 46 (p. 571). Since, with this method, the influence of contraction is neglected, the results are never really trustworthy even if the same conditions are always observed; moreover, very different results are obtained with the same products, according to the degree of dilution; the purity nearly always appears the greater, the greater the dilution in which the apparent dry substance (or degrees Brix) is determined.

¹ *Sucrierie indigène*, 1901, 57, 579.

² *Z. Ver. deut. Zuckerind.*, 1881, 31, 192.

B.—ESTIMATION OF SUCROSE.

The normal weight of the massecuite is dissolved in warm water in a tared dish, carefully transferred to a 100 c.c. flask, cooled, clarified with the necessary quantity of basic lead acetate solution (3-4 c.c.), and the rotation determined in the usual way; the same directions are followed in carrying out the inversion method.

C.—ESTIMATION OF RAFFINOSE.

This estimation is conducted as described under III., *F* (p. 607).

D.—ESTIMATION OF INVERT SUGAR.

The method described under I., *C* (p. 554), is employed. 44 g. of the massecuite are dissolved, the solution treated with neutral lead acetate solution, made up to 200 c.c. and filtered; 100 c.c. of the filtrate (corresponding to 22 g. of massecuite) are then treated with 10 c.c. of sodium carbonate solution, filtered, and 50 c.c. of the filtrate (corresponding to 10 g. of massecuite) used for the estimation.

E.—ESTIMATION OF WATER.

The method described under IV., *A*, is employed. The quotient of purity is calculated according to II., *C* (p. 587).

F.—ESTIMATION OF ASH.

For this estimation 3 g. of the massecuite are incinerated according to Scheibler's method (*cf.* II., *D*, p. 589).

G.—ESTIMATION OF ALKALINITY.

For this purpose 10 g. of the massecuite are used in very dilute solution, according to II., *F* (p. 591).

The estimation of lime is carried out as described on p. 592.

H.—COLOUR.

For this estimation see II., *G* (p. 592).

I.—ESTIMATION OF THE CONTENT OF CRYSTALS.

Owing to the difficulty of execution and to the length of time required, none of the various indirect methods¹ which have been proposed have found a general acceptance in practice. The experimental centrifuge is considered the best method of estimation, since it allows of the separation of syrup and crystals under the same conditions as obtain in the factory work, furnishes the crystals in any desired state of purity (as raw sugar or white crystal sugar), and renders a direct weighing possible.

In many factories the separation of the syrup and crystals is effected by suction instead of by centrifuging, whilst in others it is found sufficient to separate the syrup from the crystals, as far as possible, by means of wire sieves.

V. SUGAR.

(Raw Sugar, Refined Sugar, After-products.)²

A.—ESTIMATION OF SUCROSE.

The normal weight (26 g.) of the thoroughly mixed sample is dissolved in the tared dish in warm water³ and transferred to a 100 c.c. flask. In the case of raw sugars and after-products, the cooled solution is clarified by addition, drop by drop, of basic lead acetate solution (about 1 c.c. for first and 2-3 c.c. for after-products), and then treated with about 1 c.c. of alumina cream; in the case of refined sugars, the cooled solution is treated only with 3-5 c.c. of alumina cream. This is prepared, according to Scheibler's method, as follows:—A not too concentrated solution of aluminium sulphate or alum is treated with excess of ammonia, and the precipitate washed by decantation or syphoning, until all the salts and ammonia have been removed. The pure homogeneous cream thus obtained is stored in well-stoppered bottles, and thoroughly shaken before use. According to Baumann,⁴ alumina cream may be readily obtained in a pure state by the electrolysis of water between aluminium electrodes.

After clarification, the sugar solution is made up to the mark at 20° (any froth being removed by ether vapour or 1-2 drops of

¹ *Z. Ver. deut. Zuckerind.*, 1894, 44, 892.

² See the *Arbeitsvorschrift* of the Institut für Zuckerindustrie.

³ According to the decisions of the Austro-Hungarian Sugar Chemists, solution must not be effected with the aid of heat.

⁴ *Korrespondenzblatt*, 1893, No. 10.

absolute alcohol), mixed, filtered, and the rotation determined in a 200 mm. tube at the same temperature.

In presence of raffinose or of invert sugar in large quantity, the true content of sucrose is found by the optical inversion method as described above (p. 607).

B.—ESTIMATION OF WATER AND NON-SUGAR.

5 g. of the sugar are weighed into a tared nickel dish, and dried for two to three hours *in vacuo* at 110° until the weight is constant.

The total content of non-sugar is obtained by deducting the sum of the percentages of sugar and water from 100.

A method for the estimation of water by means of the Immersion Refractometer has been proposed by Stanek.¹

C.—ESTIMATION OF ASH.

3 g. of the sugar are incinerated according to Scheibler's method (see p. 589). By deducting the ash-content from the total non-sugar-content, the content of organic non-sugar is obtained.

In order to estimate the actual proportion of ash in cases where the sugar (especially after-products) contains appreciable quantities of mechanical impurities, a weighed portion of the sample is dissolved in a known quantity of water, the solution filtered, an aliquot part of the filtrate evaporated in the incinerating dish, and incinerated after addition of sulphuric acid. If desired, the solution may be filtered through a tared filter and the residue weighed. In commercial analyses, however, no special attention is paid to the mechanical impurities.

D.—ESTIMATION OF INVERT SUGAR.

This estimation is carried out according to the methods described under I., C (pp. 554 *et seq.*); a content of less than 0.05 per cent. of invert sugar cannot be determined with certainty.

In Austria-Hungary, conformably with the previously mentioned Report, the qualitative detection of invert sugar in raw sugars is effected with Soldaini's solution as follows:—10 g. of the sugar are dissolved in 25 c.c. of water, treated with 100 c.c. of the copper solution, and boiled for five minutes (reckoned from the commencement of boiling). Soldaini's solution is prepared by dissolving 15 g. of precipitated copper carbonate and 416 g. of potassium bicarbonate in

¹ *Z. Zuckerind. Böhm.*, 1910, 35, 57.

1400 c.c. of water, or by adding the corresponding quantity of copper sulphate to the potassium bicarbonate solution.¹

E.—ESTIMATION OF RAFFINOSE.

The content of raffinose is calculated from the formula given on p. 608, after the sugar has been inverted. According to Herzfeld,² the employment of the raffinose formula must be confined to those sugars in which the presence of raffinose may be expected with good reason, and preferably therefore to the products resulting from the molasses desaccharification; further, this method is not applicable to the estimation of raffinose by means of the simple inversion method in products containing more than 2 per cent. of invert sugar.³

F.—COLOUR.

For this estimation see under II., G (p. 592).

G.—ESTIMATION OF ALKALINITY.

Every raw sugar should show a perceptibly alkaline reaction towards phenolphthalein, or at any rate towards litmus, since, as a rule, the keeping properties and suitability for storage of neutral or acid reacting sugar are very small, and serious loss may easily occur if such raw sugars are required to be stored for a long time.

The qualitative test may be effected by placing a few crystals on red litmus paper, and moistening them with water; a distinct blue coloration should appear at the moistened part. The examination with phenolphthalein is more sensitive since many raw sugars which show an alkaline or neutral reaction to litmus are acid to phenolphthalein, whereby their inferior quality is demonstrated. The quantitative estimation of alkalinity is seldom required; it is effected by titrating a solution of 10 g. of the sugar in a considerable quantity of neutral water with *N*/28 acid.

With regard to the special trade customs of various countries, in Austria-Hungary the use of litmus as indicator, and a statement as to whether the sugar is alkaline, acid, or neutral, is prescribed.⁴ In Germany at the present time a method worked out by Herzfeld,⁵ and agreed to by sugar manufacturers and merchants, is employed.

¹ *Z. Ver. deut. Zuckerind.*, 1889, 39, 933; 1890, 40, 792.

² *Ibid.*, 1890, 40, 167.

³ Cf. the *Ausführungsbestimmung z. Zuckersteuergesetz*, v., 27th May 1896, § 2, Section 5, and Appendix B, II.

⁴ *Oesterr.-Ungar. Zeitschr.*, 1901, p. 666.

⁵ *Z. Ver. deut. Zuckerind.*, 1902, 52, 115; cf. *ibid.*, 1907, 57, 246.

H.—EXAMINATION FOR SULPHUROUS ACID.

Sulphurous acid is often used for the decolorisation or purification of beetroot juice, with the result that smaller or larger quantities of sulphites not infrequently occur in raw sugar, while sometimes even free sulphurous acid is present. If an examination for these compounds is required, 10 g. of the sugar are dissolved in about 30 c.c. of water and a small piece of chemically pure zinc or some magnesium wire is added, together with 5 c.c. of chemically pure hydrochloric acid; if sulphurous acid is present, sulphuretted hydrogen is then evolved, which may often be detected by its odour and always by the production of a brown stain on a piece of filter paper moistened with a solution of acetate of lead; a blank experiment, in which no sugar is used, serves as a control. According to Davidson,¹ 1-1.5 g. of sugar is dissolved in about 2 c.c. of very dilute starch solution and a few drops of iodic acid solution added; the appearance of a blue coloration indicates the presence of sulphurous acid.

Sachs² estimates the sulphites quantitatively by the following modification of the method devised by Pellet:—100 c.c. of the 10-15 per cent. solution are treated with some acetic acid and a few centigrams of sodium bicarbonate; the solution is then titrated with a solution of iodine (1 c.c. = 0.01 g. of iodine), starch solution being used as indicator. The amount of iodine required is assumed to be equal to that of the sulphite (since 127 g. of iodine correspond to 126 g. of sodium sulphite). As a control, a parallel experiment is made with a substance known to be free from sulphite.

I.—ESTIMATION OF THE CONTENT OF CRYSTALS.

The methods described under IV., I (p. 613), are applicable. The uniformity, or variation, of the size of the crystals may be determined quantitatively by means of a standard series of sieves.

Koydl's washing method,³ which is very well worth consideration, has not yet found application in practical working on the large scale.

K.—CALCULATION OF YIELD (RENDEMENT).

By "rendement" or refining value is understood a number which represents the quantity of crystallised white sugar obtainable on refining a raw sugar. Although it is a fact that the determination of the so-called "rendement" possesses no scientific or technical

¹ *Deutsche Zuckerindustrie*, 1887, 12, 939; *J. Soc. Chem. Ind.*, 1887, 6, 681.

² *Oesterr.-Ungar. Zeitschr.*, 1901, p. 366.

³ *Ibid.*, 1906, 35, 277; 1908, 37, 634.

value, yet in commerce the so-called "ash rendement" is generally retained. This rendement is calculated by deducting five times the weight of ash from the polarisation, and hence the assumptions are made that the ash alone has a melassagenic action, that 1 part of ash prevents 5 parts of sugar from crystallising, and that neither the physical properties of the raw sugar, nor the method of refining it, has any influence on the yield. All these suppositions are generally acknowledged to be inaccurate, and the ash rendement is only retained by the trade because sugar and ash may be estimated quickly and without great discrepancies.

Any invert sugar that may be present is also considered in the calculation of rendement; the factors with which it is multiplied, previous to deduction from the ash rendement, differ in various localities, and are generally likewise quite arbitrary.

The so-called "new rendement," the calculation of which is effected by deducting from the polarisation the product (total non-sugar $\times 2.25$), has not found acceptance in commerce.

VI. MOLASSES. RUNNINGS. MOTHER SYRUPS.

A.—DETERMINATION OF THE SPECIFIC GRAVITY.

The pyknometer is used for exact determinations of the specific gravity. Before the sample is introduced into the pyknometer it is necessary to remove mechanical impurities of all kinds from the sample, and, by warming it (in the case of mother syrups this is done after the syrup has been freed from the massecuite by suction), to render it free from air and sufficiently mobile. For this purpose a funnel closed with a glass rod is used. The funnel is filled with the molasses and suspended in a suitable vessel filled with boiling water; after a short time the molasses becomes mobile and the occluded air-bubbles rise to the surface where they form a tough, thick scum with the bulk of the impurities, whilst sand particles, etc., sink to the bottom. After, at most, thirty minutes, the funnel is removed from the water-bath, and, after the first runnings have been thrown away, the molasses is allowed to flow in a thin stream into the previously slightly warmed pyknometer. In order to avoid evaporation of water during the protracted heating of molasses containing much air, a double-walled copper de-aëerator, provided with an outflow-cock and a cover, has been used with satisfactory results.¹

By using a 50 c.c. flask as a pyknometer, the determination of the specific gravity may be effected by Sidersky's method described above

¹ Cf. *Korrespondenzblatt*, 1893, No. 9.

(p. 611). For the special purpose in question J. C. Boot¹ has proposed the following modification:—The 50 c.c. flask, after the molasses has been introduced and allowed to cool, is filled to the mark, not with water, but with a solution of potassium carbonate containing 35.45 per cent. of the salt (sp. gr. 1.400); the flask and contents are then weighed. The weight of the contents multiplied by 2 gives directly the specific gravity of the molasses, the result being the more accurate the less it differs from the roughly average value of 1.400.

Genieser's method² furnishes results of scientific accuracy. It avoids the preliminary de-aëration of the molasses and the inaccuracy of measuring, since the molasses, uniformly heated, and freed from impurities by filtration through wire gauze, is de-aërated in small flasks and the quantity of water with which the flask is filled up after the introduction of the molasses is determined, not by measuring, but by weighing. The water evaporated during de-aëration introduces no error, since the flask is finally filled up with water and the increase in weight compared with that of the original, not heated molasses.

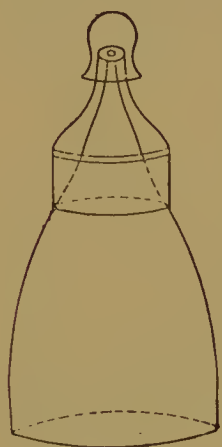


FIG. 68.

Baumann³ recommends Genieser's method, with the employment of a special form of pyknometer⁴ (Fig. 68). This is a cylindrical flask of about 30 c.c. capacity, closed by means of a perforated glass stopper which is narrowed at the top to a capillary about 2 cm. long. A small ground-glass cap is placed over the stopper. In order to determine the capacity of the pyknometer, it is filled, after removing the stopper, with water at 20°; the stopper is then replaced, whereby the excess of water is removed and the capillary becomes filled with

water; the water at the top of the capillary is then wiped off carefully, the stopper covered with the cap, and the pyknometer dried and weighed. The dry, empty pyknometer is then filled to $\frac{1}{2}$ - $\frac{2}{3}$ with molasses (not previously freed from air), weighed, and placed in a boiling water-bath in order to remove air-bubbles. The heating in a brine bath until the molasses boils, as Genieser recommends, is not advisable, on account of the possibility of decomposition. As soon as the syrup is free from air-bubbles, and there is only a slight froth on the surface, it is cooled to the normal temperature, the pyknometer filled with water at 20°, stoppered as described above, and weighed, the volume of the molasses being calculated from the result. The degrees Brix or Baumé corresponding to the specific gravity thus found may be obtained from Table 46 (p. 571); since the non-sugar substances

¹ *J. Soc. Chem. Ind.*, 1897, 16, 415.

² *Deutsche Zuckerindustrie*, 1890, p. 168.

³ *Korrespondenzblatt*, 1891, No. 1.

⁴ The pyknometer may be obtained from the Vereinslaboratorium, Berlin.

contained in the molasses seriously affect the result, the use of this Table, compiled for pure sugar solutions, is of course arbitrary and quite conventional.

The estimation of the dry substance or of the specific gravity by means of the Abbé refractometer cannot always be effected directly with very dark products, since the reading is rendered difficult by the colour of the solution; dilution of the molasses or syrup, best to double the weight, is necessary in such cases.

The contraction which occurs on dilution with water is often sufficient to invalidate the results. According to Tischtschenko,¹ this difficulty may be avoided by using a solution of pure sugar of about 50 per cent. concentration instead of water, since a mixture of, say, equal parts of molasses and 50 per cent. sugar solution is not only always sufficiently light in colour, but also possesses a correspondingly increased purity, which is a further aid to accuracy; of course, in calculating the result, allowance must be made for the amount of added sugar.

The determination of the degrees Brix by the convenient but less accurate "dilution method," which is sufficient for many purposes, is effected in the same way as in the case of massecuites (p. 611).

B.—ESTIMATION OF SUCROSE.

(a) For direct polarisation, half the normal weight (13 g.) is weighed into the tared nickel dish, stirred with warm water, and then rinsed into a 100 c.c. flask. For clarification, at least 7-8 c.c. and often 10 c.c. of basic lead acetate solution are required. After the solution has been made up to volume, it is mixed, filtered, and the rotation determined; the reading is multiplied by 2.

(b) The estimation of the true content of sucrose in the presence of invert sugar and raffinose is carried out by the Clerget method of polarisation before and after inversion, as described under III., B (pp. 597 *et seq.*). The formulæ requisite for the calculation are given in Table 50, C (p. 600).

If the molasses (and similar substances) contains large quantities of certain salts, especially organic salts, it may happen that the complete inversion by the usual method is not effected within five minutes; in such cases, according to Henze,² the quantity of hydrochloric acid is increased to 6 c.c., and the temperature, according to Koydl,³ is raised to 75°-80°.

For low-grade molasses and other products containing a large proportion of non-sugar substances, Andrlík and Stanek, Pellet and Ogilvie have proposed methods according to which an acid solution is

¹ *Z. Ver. deut. Zuckerind.*, 1909, 59, 103.

² *Deutsche Zuckerindustrie*, 1900, p. 1830.

³ *Oesterr.-Ungar. Zeitschr.*, 1900, p. 403.

used for the polarimetric reading before as well as after inversion. These are described in the following pages.

The use of invertase as hydrolyst in place of hydrochloric acid has been frequently suggested.¹ Working with dark coloured after-products, which must be defecated with basic lead acetate after inversion, an error is introduced by the precipitation of some of the lævulose as lead compound. Ogilvie² has described a method which obviates this. It is carried out as follows:—Four times the normal weight of the sample is dissolved in water, defecated with the minimum quantity of basic lead acetate solution, and treated with a small quantity of alumina cream. The whole is made up to 200 c.c. at 20°, mixed and filtered; 100 c.c. of the filtrate are then treated with a current of sulphur dioxide until a faint odour is perceptible (the indication that all the lead is precipitated), made up to 200 c.c., mixed, treated with sufficient dry calcium carbonate to neutralise the excess of acid, and then with a little recently ignited kieselguhr, and filtered. A normal solution is thus obtained which is sufficiently clarified to give a distinct polarimetric reading. For the inversion process, 50 c.c. of the clarified solution is heated in a constant temperature bath to 50°-55°, treated with 0.5 g. of washed brewery yeast (top fermentation), and two drops of acetic acid, the whole being kept as nearly as possible at 55° for four and a half to five hours. The liquid is then cooled, treated with a little alumina or kieselguhr, made up to 100 c.c., mixed and filtered, and the rotation of the filtrate determined at 20°. The inversion polarisation obtained by Ogilvie when working with pure sucrose was -31.6° V., whereas Ling and Baker (*loc. cit.*) obtained the same constant as Herzfeld obtained by the acid method, viz., -32.66° V. Although the invertase method takes up more time than the acid method, it necessitates no more personal attention. It will be convenient here to give a description of some recent modifications of the Clerget process which have been applied to both beet and cane molasses.

Pellet in 1897³ proposed to remove the lead in the direct polarisation liquid by sulphurous acid in slight excess, whilst Andrlík and Stanek in 1906⁴ proposed to add to the direct polarisation liquid the same quantity of hydrochloric acid as is present in the inverted solution, together with a certain amount of urea or betaine to retard the hydrolysis of the sucrose by the hydrochloric acid. One objection to this method is that quite an appreciable amount of hydrolysis occurs under these conditions even two minutes after the preparation of the

¹ Kjeldahl, *Res. Compt. rend. Lab.*, Carlsberg, 1881, 1, 192; O'Sullivan and Thompson, *J. Chem. Soc.*, 1891, 59, 46; Ling and Baker, *J. Soc. Chem. Ind.*, 1898, 17, 111; C. S. Hudson, *U.S. Dep. Agric., Bureau of Chemistry*, 1910, Circular No. 50, p. 1.

² *J. Soc. Chem. Ind.*, 1911, 30, 62; *Int. Sugar J.*, 1912, 14, 89.

³ *Bull. Assoc. Chim. Sucr.*, 15, 524.

⁴ *Z. Zuckerind. Böhm.*, 31, 417.

solution, and a second objection to the method has reference to the effect of the bases employed by Andrlík and Stanek on the rotation of reducing sugars when present. In the case of beetroot molasses, which do not contain reducing sugars, or at the most only traces, this method appears to give results which agree well with those obtained by the Pellet method.

Ogilvie¹ has compared the results obtained with invertase and acid hydrolysis respectively in the case of five samples of cane molasses, and arrives at the following conclusions:—(1) The percentage of sucrose found by the acid inversion process usually employed when the direct polarisation is taken in alkaline solution are too high.² (2) The percentage of sucrose found when using a neutral direct polarisation liquid may likewise be too high. (3) The values found when using an acid direct polarisation liquid are in close agreement with those obtained by the invertase method.

Ogilvie's results with beet and cane molasses are given in the Tables on p. 622.

In a more recent paper Ogilvie³ has modified the Pellet method of removing the lead from the direct polarisation liquid by means of sulphurous acid, and has applied it to the estimation of sucrose in beet molasses by the Clerget process. His procedure is as follows:—Twice the normal weight is dissolved in water, defecated with basic lead acetate, and made up to 200 c.c. with water. 50 c.c. of this solution are transferred to a 100 c.c. flask, saturated with sulphur dioxide, the flask being immersed in cold water meanwhile, and subsequently made up with water to 100 c.c. and filtered. For the inversion solution 50 c.c. of the defecated normal solution of molasses are transferred to a 100 c.c. flask, 25 c.c. of water added, and 5 c.c. of hydrochloric acid (sp. gr. 1.19), and treated according to Herzfeld's directions (see p. 597). Working under these conditions, it is shown that the direct polarisation liquid may be kept for thirty minutes without showing any diminution in rotation.

Molasses (and similar substances) which contains a large quantity of raffinose cannot, as a rule, be examined without decolorisation by purified bone or blood charcoal. According to the investigations of Reinhardt⁴ and Wiske,⁵ owing to certain absorption phenomena,⁶ this addition often causes considerable differences which must be allowed for. This error is compensated empirically by a method which is

¹ *Int. Sugar J.*, 1912, 14, 91.

² Exactly the opposite result was obtained by Ogilvie when working with beet molasses, which, however, as he points out, has a different composition from the cane product. In the former the disturbing factor is the presence of amino-acids, whilst in the latter it is the presence of reducing sugars.

³ *Int. Sugar J.*, 1912, 14, 624.

⁵ *Ibid.*, 1902, 52, 945.

⁴ *Z. Ver. deut. Zuckerind.*, 1902, 52, 114.

⁶ Lippmann, *Chemie der Zuckerarten*, p. 1660.

sufficiently accurate for practical purposes, as follows:—For a content of raffinose up to 3 per cent. and independently of the sugar-content of the solution, 0.1 per cent. for each 1 per cent. of raffinose is deducted from the lævo-rotation after inversion. It is assumed that 3 g. of pure charcoal are in contact for five minutes with a solution containing half the normal weight.

Beet Molasses.

Sample.	1	2	3	4
Direct alkaline (basic lead acetate) polarisation	48.8	...	48.6	47.0
Direct neutral polarisation	49.2	52.0	49.0	47.6
Direct acid (Andrlik) polarisation	50.4	53.25	50.0	48.4
Direct acid (Pellet) polarisation	50.3	53.3	...	48.3
Invertase inversion polarisation	-14.6	-16.0	-15.0	-14.4
Acid inversion polarisation	-13.2	-14.6	-13.6	-13.8
Clerget value by invertase	48.5	51.7	48.6	47.1
Clerget value by acid, using alkaline direct polarisation	47.0	...	47.1	46.1
Clerget value by acid, using neutral direct polarisation	47.3	50.5	47.4	46.5
Clerget value by acid, using acid (Andrlik) direct polarisation	48.2	51.4	48.2	47.1
Clerget value by acid, using acid (Pellet) direct polarisation	48.1	51.4	...	47.0

Cane Molasses.

	Cuban molasses.		Egyptian molasses.	Javan molasses.	"American syrup."
	No. 1.	No. 2.			
Ash (sulphated)	6.77	7.34	10.92	10.97	6.05
Reducing sugars	18.71	18.56	11.70	21.98	26.55
1. Alkaline (basic lead acetate) polarisation	32.20	31.40	39.50	34.30	39.70
2. Neutral direct polarisation	30.50	29.90	38.10	33.46	39.65
3. Acid (HCl and urea) polarisation (Andrlik)	30.50	30.50	38.40	33.38	39.26
4. Acid (SO ₂) direct polarisation (Pellet)	30.60	30.50	38.30	33.30	39.10
5. Invertase inversion polarisation	-16.40	-15.50	-17.90	-14.08	-11.40
6. Acid inversion (Herzfeld) polarisation	-16.30	-15.40	-18.02	-14.06	-12.28
7. Percentage of sucrose, using invertase as hydrolyst	35.6	34.4	42.4	36.1	38.7
8. Percentage of sucrose, using acid as hydrolyst, and the alkaline direct polarisation	36.7	35.4	43.4	36.6	39.3
9. Percentage of sucrose, using acid as hydrolyst, and the neutral direct polarisation	35.4	34.2	42.4	35.9	39.2
10. Percentage of sucrose, using acid as hydrolyst, and the acid (HCl and urea) direct polarisation (Andrlik)	35.4	34.7	42.6	35.9	38.9
11. Percentage of sucrose, using acid as hydrolyst, and the acid (SO ₂) direct polarisation (Pellet)	35.5	34.7	42.5	35.8	38.8

The use of basic lead nitrate as a clarifying agent is referred to under "Osmose Water" (p. 632).

C.—ESTIMATION OF WATER AND OF NON-SUGAR SUBSTANCES.

The "true" content of dry substance is determined in the same way as in massecuites, 50-75 g. of sand being used for 2-3 g. of substance.¹ The difference between the content of dry substance and that of sugar represents the total non-sugar. Concerning the calculation of the "true" and "apparent" quotients of purity, *cf.* II., C (p. 587). The refractometric method for determining dry substance is described above under III., C (p. 600).

According to the official methods of the German Sugar Customs, for sugar syrups which contain less than 2 per cent. of invert sugar, the value calculated from the polarisation and the specific gravity (determined by the dilution method, p. 611), or the corresponding degrees Brix, serves as quotient for Customs purposes. If the syrup contains 2 per cent. of invert sugar or more, the degrees Brix must be calculated from the specific gravity of the undiluted syrup found by means of the pycnometer, whilst the total sugar found by the gravimetric inversion method (Table 44, p. 562) is taken to represent the sugar-content in making the calculation. Finally, in the case of syrups containing raffinose, the sugar-content as found by Baumann's method (see III., F, p. 607) is to be used in making the calculation.

D.—ESTIMATION OF ASH.

As a rule, the estimation of ash is effected according to the expeditious sulphate method, 2 g. of the substance being used; after addition of sulphuric acid, it is advisable in many cases to dry the mixture for twenty-five to thirty minutes at 100°-130° prior to incineration. If more accurate results are required, the carbonate method, which of course takes considerable time, is preferable, about 10 g. of the sample being used.

If the estimation of any or all of the constituents of the ash is required, the usual analytical methods of separation must be used.

E.—ESTIMATION OF INVERT SUGAR.

For this purpose, the method described under I., C, pp. 549 *et seq.*, is applicable; special reference is directed to the employment of 5 g. of molasses and the use of Baumann's Table (p. 558).

In Germany² the accepted method for the determination of invert sugar in molasses and syrups is that of Baumann, 5 g. of substance being used and the percentage found from the corresponding Table. The solution is neutralised with acetic acid, clarified with neutral

¹ *Cf.* Freist, *Zentralbl. für Zuckerind.*, 1909, 17, 883.

² *Z. Ver. deut. Zuckerind.*, 1909, 59, 487.

lead acetate solution, and freed from lead with a solution of sodium carbonate.

F.—ESTIMATION OF RAFFINOSE.

This is effected according to III., *F* (p. 607); with regard to decolorisation, see under *B* (p. 597).

G.—COLOUR.

For this determination, see II., *G* (p. 592).

H.—ESTIMATION OF ALKALINITY.

Besides the ordinary methods, Strohmer¹ recommends the following, which is very serviceable, especially in doubtful cases:—15-20 g. of the sample are dissolved to 125 c.c. of water and 25-50 c.c. of the solution, according to the colour, are measured into a narrow graduated cylinder provided with a ground-glass stopper. To this solution, 1-2 c.c. of litmus tincture and 1-2 c.c. of ether (for the removal of froth formed on shaking) are added. If the cylinder is held in a horizontal position over a sheet of white paper and then oscillated gently, the solution will appear blue or bluish-green (greyish-green with dark or caramelised molasses) if the syrup is alkaline. The titration is effected with *N*/10 acid, or with *N*/5 or *N*/2 acid in the case of dark solutions; the colour-change is quite distinct.

VII. PRODUCTS OBTAINED IN WORKING UP MOLASSES.

With the exception of the osmose process, all methods of de-saccharifying molasses depend on the precipitation of the sucrose in a state of combination with metallic oxides. Besides the lime process, precipitation with strontia is also used, and indeed to a much greater extent, whilst the baryta and lead processes recently proposed have only been occasionally employed hitherto.

A.—CALCIUM SUCRATE AND WASTE LIQUORS.

1. Calcium Sucrate.

The crude product obtained in the lime process for de-saccharifying molasses is called "molasses lime," whilst the purified products are known as sucrate of lime and sugar lime, or sugar milk of lime. The methods of examination are the same for all these products.

(a) **Determination of Specific Gravity.**—It is obvious that this

¹ *Jahr- und Adressenbuch der Zuckerfabriken Oesterreich-Ungarns*, 1909-10, p. 88.

determination can only be made in the case of sugar milk of lime. The pyknometric method is employed, using a 50 c.c. flask.

(b) **Estimation of Sucrose.**—Half the normal weight of sucrate, or the full normal weight of sugar milk of lime is weighed into the tared dish, rinsed with water into a 100 c.c. flask, and treated with a few drops of phenolphthalein, whereby the contents of the flask are reddened. To effect the decomposition of the sucrate, concentrated acetic acid is now added gradually (preferably drop by drop) until the red colour disappears, the flask being continuously shaken during this addition. Any slight excess of acetic acid is approximately neutralised with a solution of sodium carbonate; the solution is then clarified with basic lead acetate solution, made up to the mark, filtered, and the rotation determined.

(c) **Estimation of Lime.**—For this estimation, 5 g. of the sucrate or 10 g. of the sugar milk of lime are stirred with about 150 c.c. of water in a capacious porcelain dish, and, after the addition of a few drops of litmus or phenolphthalein solution, titrated with $N/1$ hydrochloric or nitric acid ($N/1$ sulphuric acid must not be used, since this would precipitate calcium sulphate). 1 c.c. of $N/1$ acid is equivalent to 0.028 g. of lime (CaO). According to Taegener,¹ certain impurities derived from the limestone often vitiate the results; in order to remove these, the sucrate is boiled for fifteen minutes with 100 c.c. of water, then filtered, the filtrate boiled again, treated with a known quantity of $N/2$ hydrochloric acid in excess, and the excess of acid titrated back with $N/2$ sodium carbonate solution.

(d) **Estimation of Purity.**—By the purity of the sucrate is understood the percentage of sucrose in the dry substance remaining after precipitation of the lime. For its estimation, a large quantity of the sucrate (200-300 g.) is stirred with 500 c.c. of water, decomposed with carbon dioxide, heated on the water-bath until the calcium bicarbonate produced is decomposed, and filtered. The filtrate—the saturated juice—is evaporated to a thin syrup in which the sucrose, water, and ash are estimated according to the methods given under II. (pp. 587 *et seq.*). Since the non-sugar substances present in juices of this kind exert a considerable influence on the readings of the Brix hydrometer, the apparent and true purities generally differ appreciably, and, as a rule, the former appears the higher the greater the dilution of the solution employed. Comparative values can only be obtained if the same concentration is maintained throughout.

The estimation of ash should be carried out according to the carbonate method, and the portion soluble in water, the alkali ash (carbonates, chlorides, and sulphates of the alkalis), should be determined, and also the portion insoluble in water, the lime ash (chiefly calcium

¹ *Deutsche Zuckerindustrie*, 1910, 35, 671.

carbonate formed by decomposition of soluble calcium salts of organic acids). For the estimation, 20 g. of the syrup are dried in a weighed platinum dish and carbonised at a dull red heat; the charcoal is extracted with hot water and then completely incinerated (lime ash), while the colourless filtrate is evaporated to dryness on the water-bath and the residue ignited at a low temperature (alkali ash).

The following example illustrates the calculation of the results :—

	In 100 parts of juice. %	In 100 parts of dry substance. %	Contained in 100 parts of sucrose. %
Water	73.20
Sucrose	22.80	85.10 (Co-efficient of purity)	...
Alkali ash	1.11	4.14	4.87
Lime ash	0.52	1.94	2.28
Organic non-sugar .	2.37	8.82	10.39
	100.00	100.00	...

For the purpose of calculating the composition of the original substance the assumption (which is an arbitrary one) is made that the proportion of sucrose to the non-sugar substances free from lime, in the sugar lime, is the same as that which obtains in the saturated juice.

2. Waste Liquors.

The waste liquors contain, besides small quantities of sucrose, the greatest part of the salts and organic non-sugar substances present in the molasses, and are used chiefly as manures. For the purposes of manufacturing control, the specific gravity and the sucrose content must be determined; the examination of the value for manuring purposes is mostly confined to the estimation of potash and nitrogen.

(a) **Estimation of Specific Gravity.**—This is carried out by means of the hydrometer according to II., A (p. 569). On account of the influence of the accumulated non-sugar substances, however, comparative values only are obtained.

(b) **Estimation of Sucrose.**—The normal weight (26 g.) of the lye is rinsed with water into a 100 c.c. flask, and after the addition of a few drops of phenolphthalein solution the content of sucrose estimated by the method described under VII., A, b (p. 625).

(c) **Estimation of Potash.**—50 c.c. of the lye are evaporated to dryness and incinerated, the ash taken up with water, acidified with hydrochloric acid, and the solution filtered into a 250 c.c. flask, made up to the mark, and mixed. The sulphuric acid present is

precipitated from 50 c.c. of this solution, and the potash estimated in the usual way.

(*d*) **Estimation of Nitrogen.**—For this estimation 25 c.c. of the lye are used, the estimation being made according to Kjeldahl's method.

B.—STRONTIANITE AND PRODUCTS OF THE STRONTIA PROCESS.

i. Strontianite.

This mineral constitutes an important raw material for the preparation of the strontia required in the de-saccharification process. It contains strontium carbonate as the chief constituent (80-90 per cent.) in addition to calcium carbonate, iron oxide, alumina, and substances insoluble in acids. The quantitative analysis is carried out as follows:—

(*a*) **Estimation of Moisture.**—Of the finely ground average sample, which must be selected and prepared with great care, 10 g. are dried at 110°, until the weight is constant.

(*b*) **Estimation of the Portion insoluble in Acid.**—10 g. of the substance are moistened with water in an Erlenmeyer flask and gradually decomposed with concentrated hydrochloric or nitric acid. When the evolution of carbon dioxide is finished, the contents of the flask are heated to boiling, filtered into a 500 c.c. flask, the residue washed with hot water and incinerated in a platinum dish.

(*c*) **Estimation of Oxide of Iron and Alumina.**—The filtrate from (*b*) is made up to the mark, after cooling, and thoroughly mixed. After preliminary oxidation with nitric acid (in order to make certain that all the iron is in the form of ferric oxide), the iron and alumina in 100 c.c. (= 2 g. of substance) of the solution are precipitated with ammonia and estimated together. The solution of the precipitate in dilute hydrochloric acid and reprecipitation of the iron and alumina from this solution (which now contains only a little calcium and strontium) is much to be recommended. The filtrate from this second precipitate is added to the first.

(*d*) **Separation and Estimation of Strontium and Calcium Carbonates.**—The filtrate from (*c*) is heated to boiling, treated with a solution of ammonium carbonate, the precipitated carbonates washed with boiling water, dissolved in concentrated nitric acid on the filter, and the filtrate collected in a porcelain dish. After drying and heating for one hour at 110°, the residual nitrates are moistened with a mixture of equal parts of absolute alcohol and ether, finely ground with a glass pestle, and allowed to stand for about twelve hours, absorption of water being avoided. The strontium nitrate which remains undissolved is filtered on a weighed filter, washed with ether-alcohol, dried

and weighed, and the corresponding weight of carbonate calculated from that of the nitrate (factor 0.6973). The filtrate is treated with 20 c.c. of hot water, heated for a short time on a boiling water-bath, and the calcium precipitated either as oxalate with ammonium oxalate, or as sulphate with dilute sulphuric acid in presence of alcohol.

If the estimation of strontium (and calcium) carbonate only is required, the procedure may be simplified as follows:—10 g. of the substance are rinsed with water into a 500 c.c. flask, and decomposed with concentrated nitric acid. The liquid is then heated to boiling, and treated with a slight excess of ammonia, the precipitated iron and alumina being separated as described in (c). The solution is then made up nearly to volume (500 c.c.), the loosely stoppered flask cooled, the contents then made up exactly to volume, thoroughly mixed, filtered as quickly as possible through a pleated filter, and an aliquot portion (100 c.c.) of the filtrate used for the estimation.

The carbonate and hydroxide prepared from celestine, and now much used technically, are generally examined according to the above methods, or, if the exact estimation of the strontium present as sulphide, sulphite, and thiosulphate is desired, the method suggested by W. Feld¹ is employed.

2. Ignited Ore and Residue.

(a) **Ignited Ore.**—By the term “ignited ore” is understood the product obtained by the ignition of the strontianite or of the strontium carbonate precipitated from solutions containing strontium (“white” and “brown” mud²). The examination of the ignited ore is confined to the estimation of the strontium oxide; owing to the slight solubility of strontium hydroxide in cold water the solution is effected with hot water, and as quickly as possible. For the estimation, 10 g. of the thoroughly triturated average sample are treated with 500 c.c. of hot water in an enamelled iron dish. After determining the total weight, the solution is kept boiling for a few minutes and stirred during this operation, the evaporated water replaced by addition of hot water, the solution mixed, filtered through a dry pleated filter into a dry flask, and 50 c.c. (= 1 g. of substance) of the hot filtrate titrated with $\frac{3}{4N}$ hydrochloric or nitric acid, a few drops of phenolphthalein being used as indicator. The $\frac{3}{4N}$ acid is used solely to simplify the calculation; 1 c.c. of normal acid corresponds to 0.13265 g. of crystallised strontium hydroxide, $\text{Sr}(\text{OH})_2 + 8\text{H}_2\text{O}$, so that 1 c.c. of $\frac{3}{4N}$ acid is

¹ *Chem. Ind.*, 1898, 21, 372.

² This product is mixed in the moist state with sawdust, made into bricks, dried, and burnt.

equivalent to 0.09958 g. of strontium hydroxide, which may be taken as 0.1 g. without introducing an appreciable error. Hence, if 10 g. of the substance to be titrated are employed, the number of c.c. of $\frac{3}{4N}$ acid required represents the percentage of crystallised strontium hydroxide. In the titration of the ignited ore the percentage of strontium hydroxide found must, of course, be converted into percentage of oxide (factor 0.3893).

(b) **Residue.**—The “residue I.” left on slaking the ignited ore is made into bricks again and burnt. On slaking the product, “residue II.” is left, which as a rule is not further worked up. An examination of this waste product (the moist material) is necessary for the determination of the loss of strontia; generally, estimations of the portion insoluble in acid, the iron oxide and alumina, and the lime, are also required. The quantities necessary for the individual estimations must be weighed out in rapid succession.

(α) *Estimation of Water.*—This is done according to the method given in VII., B, 1 (a) (p. 627).

(β) *Estimation of the Portion insoluble in Acid.*—10 g. of substance are boiled with dilute acid, the insoluble residue filtered off, washed with hot water, and incinerated in a platinum dish.

(γ) *Estimation of Iron Oxide and Alumina.*—These are estimated in the filtrate from (β) according to the method given under VII., B, 1 (c) (p. 627).

(δ) *Estimation of Strontium Hydroxide.*—20 g. of substance are boiled in a 500 c.c. flask for several minutes with about 250 c.c. of water; after cooling the solution—owing to the small content of strontium hydroxide, this analysis may be carried out in cold solution—it is made up to the mark, mixed, filtered through a dry pleated filter, and 250 c.c. of the filtrate (= 10 g. of substance) are used for titration with $\frac{3}{4N}$ acid.

(ε) *Estimation of Strontium and Calcium Carbonates.*—20 g. of the residue are rinsed with water into a 500 c.c. flask, treated with 25 c.c. of acetic acid, and the analysis carried out according to the simplified method described on p. 627.

3. White Salt, Brown Salt, Centrifuged Salt, and Sucrate.

The “white salt” is obtained on slaking the ignited ore, and forms, by its action on molasses in hot solution, insoluble strontium bisucrate as well as a brown-coloured mother liquor from which the “brown salt” crystallises out on cooling. The sucate, purified by treatment with pure 10 per cent. strontium hydroxide solution, decomposes in the cold

formation of crystallised yellowish-brown coloured hydroxide, which is separated as "centrifuged salt" from the sugar solution containing strontium by centrifuging.

To estimate the strontium hydroxide in these three salts, 10 g. are dissolved in boiling water in a 500 c.c. flask, the solution made up to the mark with hot water, mixed, filtered if necessary, and 50 c.c. of the hot filtrate (= 1 g. of substance) titrated with $\frac{3}{4N}$ acid.

The estimation of the sugar in the centrifuged salt (which generally contains 3-4 per cent.) is carried out on half the normal weight (13 g.) according to the method described in VII., *A* (*b*), p. 625.

The sucrate is treated in the same way as calcium sucrate, except that in the estimation of the strontia, as already mentioned, $\frac{3}{4N}$ acid is used.

4. Charred Vinasse.

After the spontaneous crystallisation of the "brown salt," and saturation with carbon dioxide ("brown mud"; *cf.* VII., *B*, 2, p. 628), the brown mother liquor from the strontium sucrate, the so-called vinasse, is practically free from strontia. This liquor is often converted, by evaporation and roasting, into carbonised vinasse, the commercial value of which is dependent on its content of potassium carbonate. In addition to this compound, the carbonised vinasse contains as chief constituents sodium carbonate, potassium chloride, potassium sulphate, potassium phosphate, and impurities insoluble in water (carbon, sand, and clay).

The complete examination of such carbonised vinasse is made by the following standard commercial method recommended by C. Heyer.¹ In connection with sampling and storage, it is to be borne in mind that the carbonised vinasse is strongly hygroscopic.

(*a*) **Estimation of Moisture.**—10 g. are dried at 110° until the weight is constant.

(*b*) **Estimation of the Portion Insoluble in Water.**—20 g. are heated with about 250 c.c. of water in an Erlenmeyer flask on a boiling water-bath for fifteen minutes; the solution is filtered hot through a dried and weighed filter into a 500 c.c. flask, the filter and contents washed thoroughly with hot water, the residue dried and weighed (carbon, sand, and clay), and then incinerated (sand and clay). The filtrate is cooled, made up to the mark, thoroughly mixed, and used for the further estimations.

(*c*) **Estimation of Total Alkali Salts.**—25 c.c. of the solution from *b* (= 1 g. of substance) are placed in each of four shallow dishes previously

¹ *Chem. Zeit.*, 1891, 15, 915, 959; *J. Soc. Chem. Ind.*, 1891, 10, 861; *cf.* also Lacombe, *Bull. Assoc. Chim. Sucr.*, 1899, 17, 82.

weighed together with glass rods, and evaporated to dryness on the water-bath. The residues are calcined, with continuous stirring on asbestos cards, and finally ignited over the naked flame until fusion just begins. The average weight of the ignited residues gives the total alkali salts.

According to Pellet,¹ carbonised vinasse from colonial molasses sometimes contains free alkali, a fact which must not be lost sight of in the analysis of such products.

(*d*) **Estimation of Potassium Chloride.**—The contents of the first dish are dissolved in hot water, and, after acidification with nitric acid, the solution is precipitated with silver nitrate or titrated with *N*/10 solution of silver nitrate (1 c.c. = 0.00746 g. KCl.).

(*e*) **Estimation of Potassium Sulphate.**—The contents of the second dish, after oxidation of lower sulphur compounds with bromine, are dissolved in hot water, acidified with hydrochloric acid, and precipitated with barium chloride solution; the weight of barium sulphate obtained multiplied by 0.7469 gives the weight of potassium sulphate contained in 1 g. of the carbonised vinasse.

(*f*) **Estimation of Potassium Phosphate.**—The contents of the third dish, after dissolving in hot water, are first precipitated with ammonium molybdate, the washed precipitate dissolved in hot ammonia, and the phosphoric acid reprecipitated as ammonium magnesium phosphate by the addition of magnesia mixture and weighed as magnesium pyrophosphate. The weight of the latter, multiplied by 1.9078 gives the amount of potassium phosphate contained in 1 g. of carbonised vinasse.

(*g*) **Estimation of Potassium Carbonate.**—The contents of the fourth dish are dissolved in hot water rinsed into a 100 c.c. flask, and, after the addition of an excess of hydrochloric acid, heated to boiling, and sufficient barium chloride solution (containing 1.047 g. crystallised barium chloride per 100 c.c.; 0.1 c.c. = 0.001 g. BaSO₄) added for the precipitation of the sulphuric acid determined in (*e*), for which purpose therefore 0.1 c.c. of the barium chloride solution is added for each 1 mg. of the barium sulphate found. After cooling, the solution is made up to the mark with distilled water, mixed, and filtered through a dry filter; the total alkali is estimated in 20 c.c. of the filtrate (= 0.2 g. of vinasse) as potassium platinum chloride. The weight of the latter multiplied by 0.2847 gives the total content of potash expressed as potassium carbonate in 0.2 g. of the vinasse. To determine the true content of potassium carbonate, the percentages of potassium chloride, sulphate, and phosphate found as in (*d*), (*e*), and (*f*), are calculated as the equivalent amounts of potassium carbonate by multiplying by 0.9269, 0.7932, and 0.9765 respectively, and are then deducted from the total percentage found.

¹ *Bull. Assoc. Chim. Sucr.*, 1899, 17, 86.

(h) **Estimation of Sodium Carbonate.**—The content of the sodium carbonate is obtained by deduction of the total potassium salts from the total alkali salts found in (c).

The calculation of the value of the carbonised vinasse, on the basis of the analytical data determined as above described, is effected by certain commercial methods which differ, however, in various localities. They possess no scientific basis, and are more or less arbitrary.

C.—OSMOSE WATER.

The examination of osmose water¹ includes the determination of the degrees Brix or Baumé, the content of sugar, and the purity. The first is best calculated from the specific gravity which is found pyknometrically by the method recommended for molasses; the error resulting from the use of Tables which are valid for pure sugar is of course considerable in this case. In the determination of the direct polarisation, it is advantageous so to choose the dilution that 100 c.c. of the clarified solution correspond to half the normal weight; as a clarifying agent, basic lead nitrate² is much to be recommended, since it clarifies and bleaches the solution very efficiently in nearly all cases. This clarifying solution (Herles) consists of a 1:2 solution of lead nitrate and a 1:20 solution of sodium hydroxide.

In the case of impure products and those containing a very high proportion of non-sugar (as is the case with many molasses, and especially with osmose liquors) the method of analysis by inversion sometimes gives very inaccurate results. In such cases it is advisable to use a method proposed by Andrlík and Stanek,³ in which two solutions containing equal quantities of hydrochloric acid are used for the determination of the rotation polarisations before and after inversion respectively; the acid practically nullifies the influence on the polarisation of the accumulated optically active amino-acids. The procedure is as follows:—Twice the normal weight of substance is dissolved in water in a 200 c.c. flask, the solution clarified by addition of 20 c.c. each of the solutions of lead nitrate and alkali (prepared by Herles' method), made up to volume, filtered, and 50 c.c. of the clear filtrate placed in each of two 100 c.c. flasks. To one flask is then added a solution prepared by dissolving 5 g. of urea (Graeger⁴ recommends 10 g.) in 6.5 c.c. of hydrochloric acid of sp. gr. 1.19 (7.5 c.c. of acid in the case of osmose water), and making up to 49 c.c. with water. The contents of the flask are then made up to 100 c.c., filtered, and the rotation determined at once or at any rate within seven to ten minutes. The presence of the urea suffices to prevent hydrolysis of the sucrose

¹ Cf. *Jahr- und Adressenbuch der Zuckerfabriken Oesterreich-Ungarns*, 1909-10, p. 86.

² See Lippmann, *Chemie der Zuckerarten*, p. 1391.

³ *Z. Zuckerind. Böhm.*, 1907, 31, 417.

⁴ *Ibid.*, 1907, 32, 57.

by the hydrochloric acid during this short time. The contents of the other flask are hydrolysed with the same quantity of hydrochloric acid and the result calculated according to the formula :—

$$S = \frac{100(P - I)}{143.5 - 0.5 t}$$

The results obtained by this method are generally from 0.9-2 per cent. higher in the case of molasses, and from 1.6-3.2 per cent. higher in the case of osmose waters, than those obtained by Clerget's method, but they are lower than those obtained by gravimetric analysis; with the last-mentioned method, it is probable that products formed by overheating and optically inactive sugar are included in the result.

If the analysis is effected according to the usual method of inversion, and basic lead nitrate solution is used as the clarifying agent, Herles' constant 133.5 must be substituted for the constant 132.66, so that for $t=20^\circ$ the equation will be :—

$$S = \frac{100K}{133.5}$$

The raffinose formula :—

$$S = \frac{0.5124P - I_{20}}{0.839}$$

is modified as follows when basic lead nitrate is used as the clarifying agent :—

$$S = \frac{(0.4724 + 0.002 t)P - I_{20}}{0.9074 - 0.003 t}$$

or, when $t=20^\circ$,

$$S = \frac{0.5124P - I^1}{0.8474}$$

The estimations of invert sugar and of alkalinity are effected according to the methods described above.

Another method for eliminating the disturbing influence of optically active non-sugar substances has been proposed by Pellet²; it is carried out as follows :—Double the normal weight of the sample is dissolved in water, made up to 200 c.c., treated with 10-15 c.c. of basic lead acetate solution, made up to 220 c.c., mixed, and filtered. 100 c.c. of the filtrate are treated with 10-15 c.c. of a saturated solution of sulphurous acid and some paper pulp, made up to 200 c.c., mixed, filtered, and the rotation determined at 20° in a 400 mm. tube; the reading, multiplied by 1.1, gives the direct polarisation. For the inversion, 50 c.c. of the filtrate are treated according to Herzfeld's method (p. 597).

¹ *Jahr- und Adressenbuch der Zuckerfabriken Oesterreich-Ungarns*, 1909-10, p. 87.

² *Bull. Assoc. Chim. Sucr.*, 1891, 9, 439, 624.

D.—MOLASSES FODDERS.

Molasses fodders vary very widely in composition, and at present there are no generally accepted standard methods for their examination. The verification of the numerous methods proposed, which in many cases have been suggested by some special requirement, must await further experiment. The chief constituents may be determined most readily as follows¹; in this connection, the extreme difficulty of sampling must be specially emphasised.

1. Estimation of Moisture.—From 5-10 g. of the substance, which is often very hygroscopic, are dried at 100°-105°, and, if possible, until the weight is constant, though, since this is seldom attained, the result is only approximately correct.

2. Estimation of Sucrose.—Frühling's modification of K. Müller's method² is as follows:—26 g. of the substance are treated with such a quantity of water as will make up, with the water present in the substance, a total of 200 g. When the substance has been thoroughly extracted by long standing and repeated agitation, the solution is filtered, 50 c.c. of the filtrate treated with 5 c.c. of basic lead acetate solution, filtered, and the rotation determined. The observed reading must be multiplied by 2.2. If any considerable quantity of invert sugar is present, it must be determined separately in the solution obtained by extracting a suitable quantity of the substance with about ten times the quantity of water.

According to Herzfeld, the following method may be used with advantage:—26 g. of the substance are digested in a 200 c.c. flask with water and basic lead acetate solution (at least 10 c.c.) at 65°-70° for forty to fifty minutes, and then treated in the usual manner; the error caused by the volume of the insoluble matter may, as a rule, be neglected for practical purposes, or it may be corrected by dissolving 26 g. of sugar in 200 c.c. together with the extracted pulp from 26 g. of substance, and the analysis corrected by the value thus found. According to a principle advanced by Scheibler, half the normal weight of substance may be dissolved in 100 c.c. and also in 200 c.c. of water respectively; from the two "polarisations," a and b , the volume of the insoluble portion is found to be $x = 100 \frac{a - 2b}{a - b}$ and the polarisation of

the half-normal weight for 100 c.c. of solution to be $P = \frac{(100 - x)a}{100}$.

If the average content of sugar in molasses is assumed to be 48.50 per cent., the amount of molasses that has been added to the fodder can be calculated approximately.

¹ See also *Oesterr.-Ungar. Zeitschr.*, 1901, 673; *Landw. Versuchsstationen*, 1901, 56, 81.

² *Landw. Versuchs-Stat.*, 1896, 47, 249.

According to Herles,¹ the normal or half-normal weight of molasses fodder is rinsed into a 100 c.c. flask with hot water, treated with 10 c.c. of basic lead acetate solution (according to Vuaflart,² this quantity is often quite inadequate for clarification and may be the source of serious errors), cooled for fifteen minutes, made up to volume, and the rotation determined. The process is performed a second time in the same way, except that half or one-quarter of the normal weight of pure sugar is added. The difference between the two polarisations, $b-a$, is not equal to the theoretical rotation, c , of the added quantity of pure sugar, being invariably appreciably more, so that the rotation, a , must be correspondingly corrected. Since $c:(b-a)=x:a$, the true value required, x , is given by the equation:—

$$x = \frac{a \times b}{b - a}$$

A refractometric method of estimation has been described by Schlicht.³

The extraction methods in the forms originally proposed by Förster⁴ and Gonnermann,⁵ and recently by Vuaflart, in which alcohol is used as the extracting liquid and the examination of the solution is effected either according to Clerget's method or gravimetrically, have not found much acceptance in practice in spite of numerous improvements. They appear to be slow, and hardly applicable to many kinds of fodder.

According to Hissink-Goes,⁶ all methods of estimating the sugar, hitherto recommended, are useless in the case of molasses fodder containing flax seeds; for the methods proposed in these special cases, the original paper must be consulted.

3. Estimation of Fat.—5 g. of the substance, finely ground and dried at 80°, are placed on a small filter and freed from sugar by very gradual extraction with cold water, the amount of water used amounting in all to about 100 c.c. The filter and residue are dried, first at a low temperature and finally at 95°, and are then extracted in a suitable extraction apparatus (*e.g.* that of Frühling⁷) for six to eight hours with anhydrous ether. The previously weighed extraction flask is subsequently weighed after evaporation of the ether and drying the extract at 100°.

4. Estimation of Nitrogen.—This is effected by Kjeldahl's method, 5 g. of the substance being used. The percentage of nitrogen multiplied by 6.25 gives the percentage of "protein." In taking this value, which is the value required for commercial purposes, the assumption is made that protein substances contain, on the average, 16 per cent. of nitrogen.

¹ *Z. Zuckerind. Böhm.*, 1908, 32, 626.

³ *Chem. Zeit.*, 1909, 33, 925.

⁵ *Deutsche Zuckerindustrie*, 1899, p. 448.

² *Journ. des fabricants de Sucre*, 1909, 50, 27.

⁴ *Ibid.*, 1899, 23, 19.

⁶ *Landw. Versuchs. Stat.*, 1904, 60, 125.

⁷ *Z. angew. Chem.*, 1900, 13, 270.

The value is therefore quite conventional, apart from the fact that the "proteins" constitute only a small part of the nitrogenous substances in molasses.

VIII. ACCESSORIES.

A.—ANIMAL CHARCOAL.

The object of using animal charcoal in the factory is to free the juices from certain non-sugar substances, viz., colouring matter, alkalis, and lime salts. When the animal charcoal has lost this power it must be regenerated by kilning.

New charcoal is valued according to its content of moisture, carbon, and substances insoluble in acids (sand and clay); the first should not be more than 7-8 per cent., and the last should not exceed a trace. The following substances are also estimated: calcium carbonate, calcium sulphate, calcium sulphide, and the organic matter. The spent charcoal is also examined for absorbed sugar, whilst charcoal liquor, which serves for the preparation of superphosphates, is usually examined for phosphoric acid only. It is also of importance to estimate the percentage of dust.

1. Estimation of Moisture.—From 15-20 g. of the carefully selected average sample are weighed into a drying bottle provided with a ground glass stopper, and dried at 130° - 140° until the weight is constant.

2. Estimation of Carbon, Sand, and Clay.—10 g. of the finely ground animal charcoal are treated with water and 50 c.c. of pure hydrochloric acid in an Erlenmeyer flask, and boiled for fifteen minutes. The residue is collected on a dry, tared filter, washed with hot water until free from acid, and dried at 110° until the weight is constant. The filter and contents are then incinerated in a platinum dish; the residue thus obtained represents the content of sand and clay, whilst the difference between this residue and the total residue represents the content of carbon.

3. Estimation of Calcium Carbonate.—As a rule, this estimation is made indirectly by estimating the carbon dioxide from the amount of which the percentage of calcium carbonate is calculated.

The estimation of the carbon dioxide may be effected by determining the loss on decomposition with acid by means of Schrötter's or similar apparatus. In sugar factory laboratories, however, Scheibler's apparatus (Fig. 69), which permits of a rapid and sufficiently accurate volumetric estimation of the carbon dioxide, is used almost exclusively. Estimations by the method of Lunge and Rittener are at least as accurate, and much more expeditious; this method is described in Vol. I., pp. 153 and 514.

Scheibler's apparatus consists of a flask, A, in which the decom-

position is effected by the action of the dilute hydrochloric acid contained in the guttapercha cylinder S. The carbon dioxide passes through the glass tube with which the ground glass stopper is provided, and then through the rubber tube r , into a thin rubber balloon, K, which is connected with the tube r , by the right-angled tube r_1 ; this

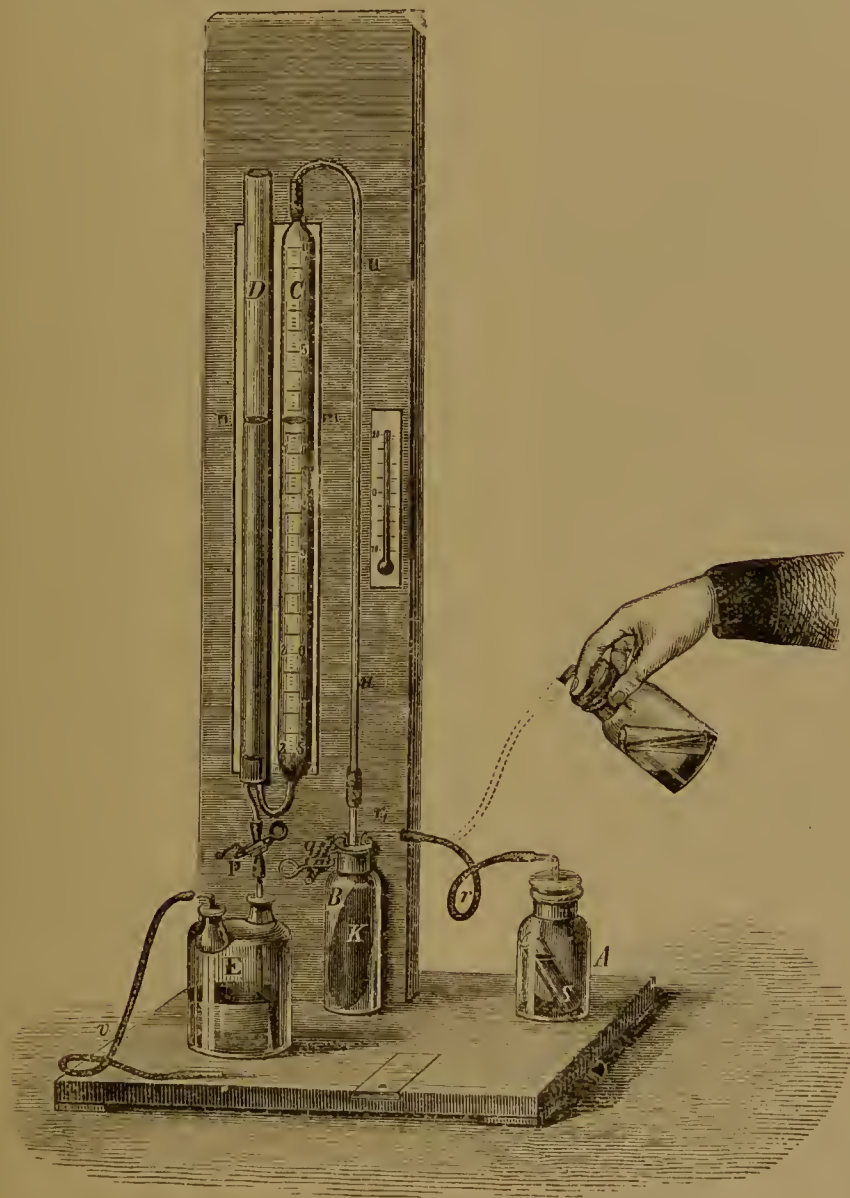


FIG. 69.

balloon is contained in the flask B, which is fitted with a stopper provided with three holes. The flask B is connected with the graduated measuring tube C by the glass tube uu , and with the external air by the tube q , which is provided with a rubber tube and pinchcock. The measuring tube C, divided into 25 Scheibler's degrees ($1^\circ = 4$ c.c.) and subdivisions of a degree, communicates at the bottom with the gas-pressure regulating tube D; the latter is also

provided at the lower end with an exit-tube which may be closed by the pinchcock *p*; this exit-tube leads to the bottom of the Woulff's bottle E, which contains water. On opening the pinchcock *p*, and blowing air through the tube *v*, the water in E may be driven into C and D. With the exception of the flask A, all parts of the apparatus are fixed by metal fastenings to a wooden stand which also carries a thermometer for observing the temperature at which the experiment is performed.

To carry out a determination, the height of the water in C is first brought to the zero point. Then connection is made with the decomposition flask A, which must be perfectly dry, in which the weighed quantity (1.7 g.) of animal charcoal as well as the guttapercha vessel filled with hydrochloric acid (2 vols. of concentrated acid to 1 vol. of water) are placed. The disturbance of the water levels in C and D caused by the insertion of the ground (thoroughly greased) glass stopper is compensated by once opening the pinchcock *q*. The flask A is then carefully tilted so as to allow the hydrochloric acid to run out slowly. The carbon dioxide evolved depresses the water in C, and raises it in D; by opening *p* at the same time the height of the water may be regulated while A is continuously kept in motion, and finally shaken, care being taken that none of the liquid in A escapes through *r* into B. As soon as no further change of volume occurs in C the water levels in C and D are exactly adjusted, and read off, together with the temperature. The percentage content of calcium carbonate is then found directly from a Table compiled by Scheibler, which is supplied with the apparatus.

The normal content of calcium carbonate in animal charcoal amounts on the average to 6.7 per cent. During use, calcium salts accumulate in the animal charcoal, and hence from time to time the content of calcium carbonate must be reduced to its normal amount. The determination of the quantity of acid requisite for the solution of the lime may be found from a Table, also compiled by Scheibler.

Thus, if 8.37 per cent. of calcium carbonate is found in a sample of animal charcoal, $8.37 - 6.70 = 1.67$ per cent. must be removed with hydrochloric acid in order to reproduce a "normal condition," e.g. of 7 per cent. Scheibler's Table shows that to effect this, 2.95 kg. of hydrochloric acid of sp. gr. = 1.17 must be used for each 100 kg. of the charcoal.

4. Estimation of Calcium Sulphate.—25 g. of the finely ground, air-dried animal charcoal are thoroughly moistened with water in an Erlenmeyer flask, and then treated with 100 c.c. of pure hydrochloric acid. When the evolution of carbon dioxide is ended, the mixture is boiled for fifteen minutes, rinsed into a 250 c.c. flask, cooled, made up to volume, mixed, and filtered through a dry filter. The sulphuric

acid in 200 c.c. of the filtrate (= 20 g. of material) is precipitated with barium chloride in the usual way, the weight of barium sulphate obtained being converted to the equivalent weight of calcium sulphate by multiplying it by the factor 0.5828.

The removal of calcium sulphate from spent animal charcoal is effected by boiling with a solution of sodium carbonate; for this purpose an excess of the latter is always used, generally about twice the calculated quantity.

5. Estimation of Calcium Sulphide.—25 g. of the finely ground, air-dried animal charcoal are treated with 0.5-1 g. of potassium chlorate, thoroughly moistened with hot water, and then treated as described under (4). From the total quantity of barium sulphate obtained the amount found in (4) is deducted; the remainder, on multiplication by the factor 0.3087, gives the equivalent quantity of calcium sulphide.

If calcium sulphide is present in considerable quantity, which only happens occasionally, the oxidation must be effected with bromine in alkaline solution according to Rössing's method.¹

6. Estimation of Organic Matter.—The qualitative examination is effected by boiling with dilute sodium or potassium hydroxide, when no brown coloration or only a very slight one should be produced. The quantitative estimation which, moreover, is always only of comparative value, is best carried out according to Drenckmann,² by titration with potassium permanganate, in the same way as in the estimation of organic matter in water.

7. The Mechanical Analysis of Charcoal.—This is carried out by estimating the amount left on sieves of various mesh. The following example of the values obtained with a good English char is given by B. E. R. and J. A. R. Newlands.³

Holes in sieves to linear inch.	Percentage of residue.
Above 10	0
10 to 20	28
20 „ 30	32
30 „ 40	27
40 „ 50	11
dust	2
	<hr/> 100

It is important that the percentage of dust should be kept low, as otherwise it occasions considerable trouble.

8. Estimation of Sucrose in Spent Animal Charcoal.—100 g. of the charcoal are boiled thoroughly four or five times successively with water,

¹ *Z. anal. Chem.*, 1902, **41**, 610. ² *Z. Ver. deut. Zuckerind.*, 1880, **30**, 733.

³ For this and other points connected with animal charcoal, cf. B. E. R. and J. A. R. Newlands, *J. Soc. Chem. Ind.*, 1888, **7**, 419. Also, *Thorpe's Dictionary of Applied Chemistry*, 2nd ed., 1912, vol. i., p. 263, article "Animal Charcoal."

a few drops of sodium carbonate solution added, the aqueous extract evaporated to a small bulk, rinsed into a 100 c.c. flask, and the rotation determined in the usual way. The polarimeter reading multiplied by 0.26 gives the percentage of sucrose in the moist charcoal. A simultaneous estimation of water in the latter allows of the calculation of the percentage of sucrose in the dry material.

Scheibler's or a similar extraction apparatus may also be used for the extraction of the sucrose from the spent charcoal.

9. Estimation of Phosphoric Acid in the Animal Charcoal Lye.—5 g. of substance are treated with 50 c.c. of nitric acid (sp. gr. 1.42) and 50 c.c. of pure concentrated sulphuric acid, and kept boiling gently for half an hour. After cooling, the whole is rinsed into a 500 c.c. flask, made up to the mark, mixed and filtered through a dry filter. The phosphoric acid is estimated in 50 c.c. (= 0.5 g. of substance) of the filtrate by precipitation with ammonium nitro-molybdate, and subsequently with magnesia mixture in the usual way. The amount of the magnesium pyrophosphate finally obtained is multiplied by the factors 0.6376 and 1.3919 respectively, in order to obtain the equivalent quantities of phosphoric acid and of tribasic calcium phosphate.

B.—STRONTIANITE AND STRONTIUM-CONTAINING MANUFACTURING PRODUCTS.

The examination of these materials is carried as described under VII., *B* (p. 627).

C.—LIMESTONE.

Limestone forms the raw material for the production of the caustic lime requisite for precipitation (precipitated lime) as well as the carbon dioxide necessary for saturation; hence great importance is to be attached to its purity, which should be of a high degree, and limestones which are considerably contaminated with gypsum, clay, silica, alkalis, etc., should never be used in sugar factories. Full details for the analysis of limestone are given in the section on the "Chlorine Industry" (Vol. I., Part I., p. 481), and in the section on "Calcareous Cements" (Vol. I., Part II., p. 659).¹

D.—DEFECATION LIME (BURNT LIME).

From the examination of the limestone used for the preparation of the defecation lime, the composition of the latter may be anticipated with sufficient accuracy. If an analysis of the precipitation lime is required, the method of procedure is the same as for limestone, the

¹ Concerning the estimation of magnesia, which often causes trouble in the filtration of the mud, see Herzfeld, *Z. Ver. deut. Zuckerind.*, 1896, 46, 204.

caustic lime being also determined as described in Vol. I., Part I., p. 484, and Vol. I., Part II., p. 669.¹ The latter determination only suffices in most cases, and in the factory the content of milk of lime is only estimated by means of a hydrometer, in conformity with Blattner's Table (Vol. I., p. 484).

For the rapid estimation of the degrees Baumé of milk of lime, Pellet² uses a 200 c.c. flask, a counterpoise corresponding to the weight of the flask filled with water, and twenty small pieces of lead corresponding to the increase in the weight for each degree between 12° and 30° Baumé. On one side of each piece of lead is marked its weight, and on the other side the corresponding degrees Baumé.

Stiepel³ has devised a very ingenious apparatus for the colorimetric estimation of caustic lime in burnt lime (see Vol. I., Part I., p. 483, and Vol. I., Part II., p. 669).

E.—WATER.

The smaller the content of dissolved matter in water, the more suitable is the latter for use in the sugar factory, since the dissolved matter tends to cause incrustation of the boilers, and it also affects the quality of the juice prejudicially. The methods for the analysis of water are fully described in the sections on "Drinking Water and Water Supplies" (Vol. I., Part II., p. 732), and "Feed-Water for Boilers, and Water for other Technical Purposes" (Vol. I., Part II., p. 799).

The water in the boilers and the feed-water must be regularly examined for alkalinity (preferably twice daily), a sudden decrease of which indicates some fault in the working, which, if neglected, may soon cause serious trouble; it is nearly always due to the presence of sugar in the condenser water (as a result of over-boiling, entrainment, etc.). As previously mentioned, the α -naphthol reaction is sufficient as a qualitative test. If the reaction obtained is appreciably in excess of the normal, a quantitative estimation is necessary. The samples taken from the vessels (preferably the collecting vessels of the continuously working drop-sampling device) are, after addition of a small quantity of a dilute solution of sodium carbonate, evaporated on the water-bath, the liquid thus obtained from a few litres of the water transferred to a 200 c.c. flask, treated with a small quantity of acetic acid (to decolorise it), clarified with about 4 c.c. of basic lead acetate solution, and finally the rotation determined in a 400 mm. tube.

¹ For a rapid method of estimating lime see Herzfeld, *Z. Ver. deut. Zuckerind.*, 1896, 46, 501. For a general method of estimating lime as oxide, hydroxide, succinate, etc., in presence of the carbonate, sulphate, etc., by means of a cold dilute solution of ammonium chloride, see Heyer, *Chem. Zeit.*, 1909, 34, 102.

² *Sucrerie Belge*, 1910, 38, 465.

³ *Z. Ver. deut. Zuckerind.*, 1901, 51, 897.

F.—SODIUM CARBONATE, SODIUM HYDROXIDE, HYDROCHLORIC ACID, SULPHURIC ACID.

Full details for the estimation of these substances are given in Volume I.

G.—SATURATION GAS, FLUE GASES.

1. Saturation Gas.

The examination of the saturation gas obtained by burning limestone or strontianite is generally confined to the estimation of the content of carbon dioxide, which may be effected rapidly and sufficiently



FIG. 70.



FIG. 71.

accurately with Stammer's burette (Figs. 70 and 71). An outlet-cock fitted to the pipe between the pump and the saturation vessels serves for taking a sample of the gas, and is connected by a rubber tube with the outlet end of the burette. The gas is drawn for a short time through the burette, the lower end of which is immersed in water, until all the air has been replaced. The burette tap is then closed and the rubber tube

detached. When the level of the water in the burette has been adjusted to the zero point, a fragment of potassium hydroxide is quickly introduced into the lower end of the tube; the latter is then closed with the thumb, and the tube thoroughly shaken. By repeatedly dipping the end of the burette in the water the latter enters the tube in place of the carbon dioxide absorbed, and from the diminution in volume the percentage of carbon dioxide in the gas may be found directly.

If it is considered desirable to estimate other constituents of the saturation gas, and in particular an abnormally high content of oxygen, which may be due either to an excessive supply of air to the lime-kiln or to a faulty pump, the gas must be removed from the part of the kiln or the pump in question by means of a powerful aspirator, and then analysed by one of the simpler methods, such as that of Hempel, as described in the section on "Technical Gas Analysis," Vol. I., Part I., p. 205.¹

For the presence of sulphurous acid in saturation gas a qualitative test only is made as a rule. For this purpose the gas is drawn through a dilute solution of iodide of starch, or through a dilute solution of indigo to which a small quantity of potassium chlorate has been added. If sulphurous acid is present, both these liquids are gradually decolorised.²

Sulphuretted hydrogen, which of course can only be present if sulphurous acid is absent, may be recognised by its odour or by the production of a brown stain on a strip of porous paper saturated with a solution of a lead salt.

If sulphurous acid is used for saturation, an analysis of the gas is not made as a rule in those factories which use the liquid acid; otherwise an estimation by means of Stammer's burette is generally considered sufficient, although owing to the great solubility of sulphurous acid in water the results are necessarily inaccurate and at the best only comparative.

2. Flue Gases.

The methods of analysis are described in the section on "Technical Gas Analysis" (Vol. I., Part I., p. 189) and under the heading "The Loss of Heat from Chimney Gases" (*ibid.*, p. 237).

The forms of apparatus for the automatic estimation of the carbon dioxide in flue gases, such as the "Sarco" Combustion Recorder, the Simmance - Abady Combustion Recorder, the "Auto" Carbon

¹ Cf. J. Seyffart, *Kesselhaus- und Kalkofenkontrolle*, 2nd edition, 1904, published by Schallehn and Wollbrück.

² Exact methods for the estimation of sulphurous acid are also given in a paper by Buisson, *Bull. Assoc. Chim. Sucr.*, 1897, 15, 146; 1899, 17, 640.

dioxide Recorder, the "Bi-meter" Carbon dioxide Recorder, and the "Autolysator" of Strache, Johoda, and Genzken may also be employed.¹

H.—FUEL.

The methods for the analysis of fuel, and the special precautions to be observed in taking samples are described in the section on "Fuel" (Vol. I., Part. I., p. 241). For the purposes of the sugar factory, comparative estimations of moisture and ash (*ibid.*, p. 242) and of sulphur (*ibid.*, p. 245) are generally considered sufficient.

IX. PRODUCTS OF THE CANE SUGAR INDUSTRY.

Despite much careful work the methods that have been proposed for the examination of the raw materials and products of the cane sugar industry lack the uniformity and precision of the methods employed in the beet sugar industry. Most of the latter are capable of being adapted to the analysis of cane sugar products, and it is for this reason, as stated at the beginning of this Section, that they have been given priority, despite the hitherto comparatively greater importance of the cane sugar industry in this country and the Colonies.

The following data are accordingly restricted to a short account of some of the proposed methods of examination and analysis that have proved satisfactory, and to sources of error associated with them. Fuller information will be found in the works on this subject included in the "Literature" appended to this Section.²

In making polarimetric estimations in tropical countries, attention must always be paid to the influence of temperature. Although, as Prinsen-Geerligs³ has shown, polarimeters obtained from Europe, adjusted at 20° with normal quartz plates, still give correct readings of these quartz plates in tropical climates at 30°, they no longer give correct readings of the equivalent normal quantity of sugar under these conditions. Thus, a normal solution of sugar reads, not +100°, but only 99.7°, so that for each $\pm 1^\circ$ there is a difference of $\pm 0.03^\circ$ in the reading. Since an alteration of the optical adjustment of the instrument would be troublesome and costly, it is best to correct the error by increasing the length of the polarimeter tubes; thus, tubes of 100.25, 200.50, and 401 mm. are to be used instead of tubes of 100, 200, and 400 mm. in length respectively. In

¹ See C. A. Keane, *The Chemical World*, 1912, I, 140, 211.

² Cf. also Prinsen-Geerligs, *7th Berichte der westjavanischen Versuchs-statik Kagok.*, 1904; *Int. Sugar J.*, 1904, 6, 380.

³ *Archiv f. d. Zuckerindustrie Javas*, 1903, II, 722.

cases where an arithmetrical correction is required,¹ Schönrock's formula,

$$P_{20^{\circ}} = P_t + P_t \cdot 0.00032(t - 20)$$

is applicable when the estimation is made at t° , and the formula,

$$P_{17.5^{\circ}} = P_t + P_t \cdot 0.00032(t - 17.5)$$

is applicable when the polarimeter is adjusted for 17.5° , and the estimation is made at the same temperature.

Areometers, hydrometers, refractometers, etc., must also be adjusted to the prevailing temperature, or must be correspondingly corrected.

I.—THE SUGAR CANE.²

Sampling.—It is extremely difficult, or scarcely possible to obtain a good average sample from the plantation such as is required for practical purposes, since even to get merely comparative results the individual samples must represent, at least approximately, the average quality of the canes in each field. It is best to take at least thirty canes from each plot, in two diagonal directions. Each cane is cut in half, and each half is cut into four pieces; the first and third piece of the first cane, the second and fourth piece of the second, and so on, are then selected. The sample which is to be crushed finally must weigh at least 8-10 kg.

Again, in sampling from carts or from vessels, which should be done during unloading, it is hardly possible, even though the utmost care be taken, to obtain really representative samples.

With regard to the examination of the material, it must be observed that no particular part of the cane can be said to possess an average sugar-content; the percentages both of sucrose and of invert sugar in any part of the cane depend on the position of the nodes and on the structure of the cane.

Estimation of Sucrose.—Of the alcoholic methods of estimation, only that of alcoholic extraction can be recommended for the direct estimation of the sucrose-content of the cane; this method, however, although it also permits of a simultaneous estimation of the woody fibre, is only rarely used. Stammer's method, which depends on the digestion of the pulp with alcohol, is not applicable, since it has not yet been found possible to prepare a pulp of the requisite degree of fineness from the cane. The method of hot alcoholic digestion also,

¹ *Archiv f. d. Zuckerindustrie Javas*, 1904, 12, 832.

² Cf. also Pellet, *Études sur la Canne à Sucre*, 1898; Krüger, *Das Zuckerrohr und seine Kultur*, 1899 (see in particular pp. 167 *et seq.*); Krüger, *Zuckerindustrie Kalender*, Leipzig, 1910, Part I., pp. 20 *et seq.*

does not yield sufficiently trustworthy results. According to Krüger, it is advisable, in the case of all those methods which involve a prolonged heating of the juice, which is often strongly acid, to add a small quantity of calcium or magnesium carbonate, in order to prevent the action of the free acid on the sucrose.

Zamaron¹ has described the following method and apparatus for directly estimating the sugar by systematic extraction with hot water. The pieces of the cane are first cut up into fine slices by means of a special machine² (*coupe cannes*), and the slices are ground to pulp in an iron mortar. 100 g. of the thoroughly mixed, and if possible, perfectly fresh pulp, are placed in the sieve-like metal basket of the apparatus, and the latter is placed in the container, the lower part of which is provided with a tap; 200 c.c. of boiling water are then poured on the pulp, the whole kept in ebullition for ten to twelve minutes, and the aqueous extract run into a 1-litre flask containing 10-15 c.c. of basic lead acetate³ solution of sp. gr. 1.24. The extraction process is then repeated, first with 200 c.c. and then with 150 c.c. of water, so that after about six extractions the volume of liquid in the 1-litre flask is about 960 c.c. The liquid is then cooled, made up to volume, mixed, filtered, and the rotation determined in a 400 mm. tube; with the Schmidt and Haensch polarimeter, the reading multiplied by 1.3 represents the percentage of sucrose in the cane. The residue in the basket may be strongly pressed with a pestle provided with the apparatus, and dried, in the basket itself, at 100°-110°; the weight of the dried residue represents approximately the percentage of woody fibre in the cane.

Pellet's method of hot aqueous digestion⁴ is carried out as follows:—The normal weight, or twice or thrice this quantity, of the finely divided cane is introduced into a 100, 200, or 300 c.c. flask, treated with 10, 20, or 30 c.c. of neutral lead acetate solution (3:10), and then made up to volume with water; a small perforated disc of lead is then placed in the flask in such a way as to prevent air-containing portions of the material from rising to the surface of the liquid. The flask is then heated for an hour, with repeated shaking, on the boiling water-bath, and allowed to cool; the leaden disc is removed, the contents of the flask made up to volume and filtered, and the rotation of the filtrate determined in a 200 mm. tube. If the normal weight of substance (26 g.) has been taken, and the solution has been made up to 100 c.c., the polarimeter reading is

¹ *Bull. Assoc. Chim. Sucr.*, 1897, 15, 74; cf. Pellet, *Études sur la Canne à Sucre*, pp. 75 *et seq.*, and for a somewhat modified form, Pellet-Chenu, p. 382.

² Dupont, *Bull. Assoc. Chim. Sucre*, 1895, 13, 292; Pellet-Chenu, *loc. cit.*, pp. 377 *et seq.*

³ Concerning the substitution of neutral lead acetate for the basic salt, see Pellet-Chenu, *loc. cit.*, p. 382 *et seq.*

⁴ Pellet, *Études sur la Canne à Sucre*, p. 87; Pellet-Chenu, p. 381.

multiplied by $\frac{100 - 2.6}{100} = 0.974$, the product representing the percentage of sucrose in the cane. It is best to make two or three determinations simultaneously, and to take the mean value of the results.

Estimation of the Dry Substance.—This may be effected on 10 g. of substance in the same way as described for the sugar beet (p. 552); owing, however, to the difficulty of expelling the water completely and to partial decomposition, the method only gives approximate results and does not permit of a trustworthy estimation of the juice-content of the cane.

As mentioned by Krüger,¹ the direct estimation of the sugar in the cane, under practical conditions, is often replaced by calculation from the sugar-content of the expressed juice, thus:—

$$\frac{\text{Sucrose in expressed juice} \times \text{juice-content}}{100} = \text{sucrose-content of the cane.}$$

The results obtained in this way are of course very untrustworthy, since the expressed part of the juice (generally amounting only to 60-65 per cent.) differs considerably in composition from the total juice, and there is no definite relationship between the compositions of the expressed part and of the total juice; moreover, the quantity and quality of the juice expressed depend on the way in which the cane has been cut up, on the intensity and duration of pressing, and on the structural nature of the portions of cane employed. Hence, in using this method, fairly comparable results can only be obtained by working always under exactly the same conditions, especially in respect of the expression of the juice. For such estimations, the roller-mill described by Fontaine,² or the press of Gallois and Dupont,³ may be recommended; the latter, which is very strongly made, is capable of dealing with 2 kg. at one time. Even with these machines, however, the calculation of the sugar-content of the cane from that of the expressed juice is still untrustworthy.

Examination of the Expressed Cane (Bagasse, Megasse).—The sampling in this case is very difficult. For the examination the above-described methods (especially the extraction or boiling with hot water and a few cubic centimetres of basic lead acetate or neutral lead acetate solution) are likewise generally used. Improved methods have been recently recommended by De Haan⁴ and by Davoll.⁵ According to De Haan's method the whole of a fairly large sample is disintegrated with a mincing machine and passed through a sieve of 7 mm. mesh

¹ *Zuckerindustrie Kalender*, 1910, p. 23; see also Pellet, *Sucrierie indigène et coloniale*, 1899, 53, 170.

² *Bull. Assoc. Chim. Sucr.*, 1895, 13, 291.

³ Pellet-Chenu, p. 379.

⁴ *Archiv für die Zuckerindustrie Javas*, 1910, 18, 118.

⁵ *Int. Sugar J.*, 1909, 11, 381.

(the whole of the material must be passed through the sieve). 20 g. of the sifted material are boiled in a tared vessel with 250 c.c. of water for fifteen minutes; the mixture is stirred during boiling, and the water lost by evaporation is replaced. The mixture is then cooled, treated with 3 c.c. of basic lead acetate solution, weighed, filtered, and the rotation of the filtrate determined in a 400 mm. tube.

According to Davoll's method, the material is disintegrated to such a degree that it will pass entirely through a wire sieve of about 10 meshes per sq. cm. 26 g. of the sifted material are extracted with 80 per cent. alcohol in the extraction apparatus for one and a half hours, the solution being made up to 100 c.c., and the rotation determined in a 400 mm. tube.

Direct estimations of the dry substance in the megasse are tedious and difficult. Indirect methods, *e.g.* those which depend on the weighing of a sampling vessel filled with bagasse according to a uniform method (a water-content found by an occasional direct determination being taken as a constant), give, at the best, comparative results sufficient for technical purposes.

II. FACTORY PRODUCTS.

All factory products should be analysed in as fresh a state as possible, and, if practicable, immediately after sampling, since the invert sugar and the readily decomposable organic non-sugar render them very susceptible to alteration, especially if they are strongly acid. This applies in an especial degree to the raw sugar, which often exhibits a considerable decrease in polarisation within a comparatively short time. The sampling of such materials, and especially of the raw sugar, is attended with great difficulty.

Estimation of Sucrose.—In the case of juices or syrups, the addition of a preservative is essential if the analysis cannot be made at once; for this purpose, pastilles of mercuric chloride (0.01 g. per 100 c.c.) have proved efficacious, though the amount of antiseptic required and the degree of stability attained can only be determined by experience. According to Pellet,¹ basic lead acetate should never be used (see below); this clarifying agent may be replaced by the neutral salt.

Even though a correction for temperature is made as described on p. 578 (a correction which of course is indispensable when the temperature differs from the normal), the ordinary rotation of cane sugar products gives values for the content of sucrose and quotient of purity

¹ *Bull. Assoc. Chim. Sucr.*, 1899, 17, 52; see, on the other hand, Maxwell, *Chem. Zeit. Rep.*, 1905, 29, 87, and de Haan, *loc. cit.*

which do not correspond to the factory conditions. According to Prinsen-Geerligs,¹ these discrepancies are chiefly due to the use of basic lead acetate; this clarifying agent causes the precipitation of lævulose with the lead precipitate from impure and especially saline solutions. Whereas comparatively small quantities of dextrose are retained in the lead precipitate, the amount of lævulose retained may amount to as much as 23 per cent. of the total quantity under certain conditions, whilst according to Pellet 40 to 80 or even 100 per cent. of the lævulose may be thrown down in the course of time at high temperatures. Lævulose is not precipitated to any great extent from mill and thin juices, which are generally fairly acid and of low saline content; it is precipitated in larger proportion from "clairce" syrups, after-products, and molasses which, moreover, on account of their dark colour, require the addition of a considerable quantity of basic lead acetate. Hence it would be desirable to abandon the use of basic lead acetate entirely, and to employ neutral lead acetate only as a clarifying agent, as has been recommended by Pellet.² (Compare, however, p. 621.) In practical working, however, the use of the neutral salt involves many difficulties, and as a rule the basic salt is considered quite indispensable, especially in view of the fact that lead nitrate does not give better results; neutral lead acetate and animal charcoal frequently do not bleach the solution sufficiently, and zinc dust is both insufficient and uncertain in its action. In order to obtain at least uniformly comparable results, Prinsen-Geerligs recommends that the quantity of basic lead acetate solution required for decolorising the molasses of the factory should be determined, and that the same quantity should be used in all analyses of the factory products; in any case, however, all the analyses must be carried out in exactly the same way.

According to Pellet, on the other hand, if the neutral acetate or the basic acetate (30 per cent. solution) rendered neutral to litmus with acetic acid does not decolorise the solution sufficiently, the rotation of the latter should be determined in a shorter tube and with a brighter light (electric or acetylene), or else it should be further clarified, and preferably with a cold solution of sulphurous acid, or freshly prepared chlorine water,³ or sodium hypochlorite or bleaching powder, and some neutral lead acetate (but not basic lead nitrate or animal charcoal, which nearly always possess the property of absorbing the sugars). Sulphurous acid has the advantage that it completely precipitates the lead remaining in solution, and that it is more suitable than any other reagent, *e.g.* sodium oxalate, proposed for this purpose.

¹ *Archiv f. d. Zuckerindustrie Javas*, 1898, 6, 914; see also 6, Supplement, p. 272.

² *Journal des fabricants de Sucr.*, 1899, 40, No. 15; *Bull. Assoc. Chim. Sucr.*, 1898, 16, 1007, 1147; 1904, 22, 744; 1907, 25, 395; *Sucrierie indigène*, 1904, 64, 67.

³ For Zamaron's method of preparation, see *Bull. Assoc. Chim. Sucr.*, 1899, 17, 52.

More recently Pellet has condemned any clarification and decolorisation.¹

According to Deer,² clarification may be effected as completely with sodium aluminate, aluminium sulphate, and a small quantity of sodium hydrosulphite, as with basic lead acetate. For the analysis, the normal weight of the sample is dissolved in 50 c.c. of water, treated with 3-5 c.c. of a 10 per cent. solution of sodium aluminate (quite free from carbonate), then with a slight excess of aluminium sulphate, and finally with 0.25 g. of sodium hydrosulphite. The solution is then made up to volume, filtered, and the rotation determined; allowance may be made for the volume (0.58 c.c.) of the precipitate.

According to Horne's investigations,³ the use of solid basic lead acetate in the analysis of all colonial products presents special advantages.

Prinsen-Geerligs and F. Sachs⁴ have recently stated that, generally speaking, no other clarifying agent is a satisfactory substitute for basic lead acetate, but that the latter should only be used in neutral or slightly acid solution and in as small a quantity as possible, and that any excess should be precipitated by a suitable reagent.

Since even if the precipitation of reducing sugars and other reducing substances be avoided by the substitution of neutral lead acetate for the basic salt, the direct polarisation of colonial products can never give correct values, Pellet⁵ and Tervooren⁶ have proposed that all products which contain reducing sugar should be examined exclusively by the inversion method. Whether this proposal will find acceptance in practice, however, appears doubtful, for although the method is a considerable improvement on those generally used, it is extremely difficult to carry out in many tropical countries where the laboratory equipment is only of a primitive kind. On scientific grounds also it may be objected that the reducing sugar of colonial products practically never consists of one substance, so that the use of the optical or chemical constants, valid only for definite chemical substances, does not appear to be justifiable.

Quotient of Purity.—With regard to this estimation (see p. 587), Pellet⁷ and Prinsen-Geerligs⁸ have pointed out that in the case of cane sugar syrups the difference between the degrees Brix and the true dry substance-content is, as a rule, considerably greater than in the

¹ *Int. Sugar J.*, 1910, **12**, 521.

² *Ibid.*, 1906, **8**, 388; 1907, **9**, 127.

³ *Bull. Assoc. Chim. Sucr.*, 1905, **23**, 635; *Z. Ver. deut. Zuckerind.*, 1909, **59**, 639.

⁴ *Zentralbl. f. Zuckerind.*, 1909, **17**, 1119.

⁵ *Loc. cit.*

⁶ *Archiv für die Zuckerindustrie Javas*, 1904, **12**, 321; according to Pellet (*Bull. Assoc. Chim. Sucr.*, 1907, **25**, 395), only neutral lead acetate is to be used for clarification, and no account is to be taken of the volume of the precipitate.

⁷ *Bull. Assoc. Chim. Sucr.*, 1895, **13**, 836; 1898, **16**, 1140; Pellet-Chenu, p. 388.

⁸ *Archiv für die Zuckerindustrie Javas*, 1902, **10**, 1093.

case of beet sugar syrups; these differences, which with a uniform method of working in the same factory generally remain fairly constant, may amount to 1-2 per cent. in the case of first product syrups, to 4-5 per cent. in the case of second product syrups, and to 7-9 per cent. in the case of molasses. Although these differences may be allowed for to a certain extent by standardising the method of analysis, it is best, according to Pellet, to determine the content of water directly if trustworthy results are required, rather than to use a hydrometric method (for which Brix hydrometers with a normal temperature of $27^{\circ}.5$ are often used)¹; the quotient would then be calculated from the results of the inversion polarisation and of the estimation of water. The latter estimation, however, also presents great difficulty.² This is partly owing to the presence of invert sugar and especially of lævulose, which begins to decompose at 95° , and also to the nature of the organic non-sugar; the latter is easily decomposed, and at the usual drying temperature forms further quantities of acid whereby the amount of invert sugar is increased. On this account Pellet recommends that the material should be neutralised with ammonia, mixed with pumice, and dried at a temperature not exceeding 102° - 103° ; in the case of molasses, however, a further loss in weight of 1-2 mg. occurs even after drying for five to five and a half hours. According to Krüger,³ cane-sugar products and especially cane juices should never be dried at a temperature exceeding 90° ; where possible, the drying should only be effected with the aid of rolls of filter paper, which, owing to their large surface, can easily take up the weighed quantity of juice, and the water may then be readily evaporated.

Drying *in vacuo* constitutes a useful method for obtaining more accurate results, though for the carrying out of a large number of analyses the apparatus required is as a rule too complicated; on this account such methods as those recommended by Drenckmann and by Thorne and Jeffers,⁴ in which the substance is dried in tubes heated by alcohol vapour to 65° - 70° and a current of carbon dioxide at a pressure of 50-80 mm. less than atmospheric pressure passed through the tube, have found no general acceptance.

As the result of his exhaustive investigations, Prinsen-Geerligs⁵ recommends that for cane sugars of about 95° rotation, the substance (5 g.) should be dried for two to three hours at 103° - 107° , whilst for inferior sugars, syrups, massecurites, etc., 3 g. of the substance are dissolved in the minimum quantity of hot water, the solution taken up

¹ Krüger, *loc. cit.*

² Cf. Gunning, "The Estimation of Water in Cane Sugars," *Z. Ver. deut. Zuckerind.*, 1894, 44, 927; *J. Soc. Chem. Ind.*, 1894, 14, 398..

³ *Loc. cit.*, p. 25.

⁴ *J. Soc. Chem. Ind.*, 1898, 17, 114.

⁵ *Archiv für die Zuckerindustrie Javas*, 1902, 10, 1089.

by two rolls of filter paper (1 m. long and 1 cm. high), and the latter then dried for four hours at 105° .

Estimation of the apparent purity of Crude Juice.—Samples for examination should be clear and free from air bubbles. Weinberg¹ has proposed the following rapid method for this estimation:—(1) From the polarisation value and the uncorrected Brix degrees determined with a hydrometer graduated at $17^{\circ}5$, the percentage of sucrose is found by means of Schmitz's Table (p. 580). (2) From the percentage of sucrose, and from the Brix degrees determined with a hydrometer graduated at $17^{\circ}5$, and corrected for temperature, the quotient of purity is calculated. If a hydrometer graduated at $27^{\circ}5$ is employed the temperature correction must be deducted in (1) and added in (2); the calculation each time is rendered unnecessary by a special Table from which the quotients may be read off directly.

Estimation of the Reducing Sugar.—Krüger gives the following method which, though much used, is not very accurate:—5 c.c. of diluted Fehling's solution are titrated, under the requisite conditions for estimating invert sugar, with the cane juice previously clarified with basic lead acetate solution and diluted; in this way the quantity of juice necessary to decolorise 5 c.c. of Fehling's solution is found. Since 1 c.c. of Fehling's solution corresponds to 2.5 mg. of invert sugar, the percentage of the latter in the juice is easily calculated.

Tervooren² uses the two following estimations for determining the composition of products containing much invert sugar:—(1) 13 g. of the substance are dissolved in water in a 100 c.c. flask, clarified with 15 c.c. of basic lead acetate solution, made up to volume, filtered, and the rotation determined in the usual way, the reading being doubled. (2) 6 g. of the substance are dissolved in water in a 250 c.c. flask, clarified with 15 c.c. of basic lead acetate solution, made up to volume, and filtered; 50 c.c. of the filtrate are introduced into a 100 c.c. flask, freed from lead and lime compounds by addition of 4 c.c. of Striegler's sodium oxalate solution,³ made up to volume and filtered; 50 c.c. of the filtrate (containing 0.6 g. of substance) are boiled for two minutes with Fehling's solution, the weight of metallic copper being determined in the usual way. All further calculation is rendered unnecessary by the use of a Table, by means of which the content of reducing substances is found directly from the rotation (10° - 60°) and the weight of copper (100-400 mg.). Quite apart from the clarification with basic lead acetate solution, which has been condemned by

¹ *Archiv für die Zuckerindustrie Javas*, 1900, 8, 248. For Kottmann and Maronier's quotient Tables, see Krüger, *loc. cit.*, p. 40.

² *Archiv für die Zuckerindustrie Javas*, 1902, 10, 897; for the Table, see Krüger, *loc. cit.*, p. 65.

³ Cf. Lippmann, *Chemie der Zuckerarten*, 1904, p. 607.

Pellet;¹ the method, of course, only gives at best comparative values, but it appears to be adequate for many practical purposes.

A more accurate method of estimating sucrose in colonial products, according to which allowance is made for the reducing power of sucrose in presence of invert sugar, has been worked out by Winter.² The conditions are so adjusted that for each 50 c.c. of Fehling's solution the quantity and dilution of the sucrose are always the same; a preliminary determination of the rotation is therefore requisite (see Table 53, p. 654). In this method, 50 c.c. of Fehling's solution are boiled with 50 c.c. of the diluted juice for two minutes, the precipitated cuprous oxide filtered off, washed, and finally dissolved in standard hydrochloric acid with the aid of potassium chlorate. The excess of hydrochloric acid is titrated with sodium hydroxide, and from the amount of the latter, which is equivalent to the quantity of hydrochloric acid required to dissolve the cuprous oxide, the value of G' (Table 54) may be found, which value, multiplied by the corresponding factor in the Table, gives the percentage of invert sugar contained in the juice. The expression,

$$\frac{\text{Invert sugar} \times 100}{\text{Cane sugar}}$$

is known as the "Invert-Sugar coefficient," and is regarded as a valuable comparative factor of the nature of different products.

In respect to all these methods it is important to bear in mind that the "reducing sugar" of cane-sugar products, which is incorrectly termed "glucose," is never a single substance, but a mixture of glucose, invert sugar and of their decomposition and altered products; the varied character of these products and the changes they undergo have been studied by Loby de Bruyn and by Ekenstein.³ Methods which assume a constant rotatory power and reducing power of the reducing sugar cannot, therefore, from these considerations, give an applicable result in each individual case; there is, however, no alternative method available, despite these defects, so that the approximate and comparative results thus obtained must be accepted.

The numerous analytical methods of a special character which are in use in the colonial sugar industry are of necessity beyond the scope of this section. They vary considerably in different countries and are dependent upon such factors as the accuracy of the methods of analytical control regarded as necessary, commercial conditions, duty regulations, fiscal conditions, etc., in relation to which scientific control only plays a secondary part.

For the analysis of **bagasse** and of **molasses** and of similar mixed

¹ *Sucrierie indigène*, 1904, 64, 67.

² See Krüger, *loc. cit.*, p. 27.

³ *Z. Ver. deut. Zuckerind.*, 1895, 45, 909, 1090; 1896, 46, 669; 1897, 47, 1026.

Table 53.¹

A Table for the Determination of the quantity of Juice and the Factors to be employed in the Estimation of the Reducing Sugar in Cane Juices. (Winter.)

Note.—H grams of juice are to be diluted to 200 c.c. after addition of basic lead acetate solution; 150 c.c. of the filtrate are treated with sodium sulphate, made up to 200 c.c. and filtered, 50 c.c. of the filtrate being boiled with 50 c.c. of Fehling's solution for two minutes. P = Rotation of the original juice; F = Factor; $F \times G'$ (see Table 54) = Percentage of Invert Sugar.

H.	P.	F.	H.	P.	F.	H.	P.	F.
80.00	10.0	6.67	57.14	14.0	9.33	44.44	18.0	12.00
79.21	1	73	56.74	1	40	44.20	1	07
78.43	2	80	56.34	2	47	43.96	2	13
77.67	3	87	55.94	3	53	43.72	3	20
76.92	4	93	55.55	4	60	43.48	4	27
76.19	5	7.00	55.17	5	67	43.24	5	33
75.47	6	07	54.79	6	73	43.01	6	40
74.77	7	13	54.42	7	80	42.78	7	47
74.07	8	20	54.05	8	87	42.55	8	53
73.39	9	27	53.69	9	93	42.33	9	60
72.72	11.0	7.33	53.33	15.0	10.00	42.11	19.0	12.67
72.07	1	40	52.98	1	07	41.89	1	73
71.43	2	47	52.63	2	13	41.67	2	80
70.80	3	53	52.29	3	20	41.45	3	87
70.18	4	60	51.95	4	27	41.24	4	93
69.57	5	67	51.61	5	33	41.03	5	13.00
68.97	6	73	51.28	6	40	40.82	6	07
68.38	7	80	50.95	7	47	40.61	7	13
67.80	8	87	50.63	8	53	40.40	8	20
67.23	9	93	50.31	9	60	40.20	9	27
66.67	12.0	8.00	50.00	16.0	10.67	40.00	20.0	13.33
66.12	1	07	49.69	1	73	39.80	1	40
65.57	2	13	49.38	2	80	39.60	2	47
65.04	3	20	49.08	3	87	39.41	3	53
64.52	4	27	48.78	4	93	39.22	4	60
64.00	5	33	48.48	5	11.00	39.02	5	67
63.49	6	40	48.19	6	07	38.83	6	73
62.99	7	47	47.90	7	13	38.64	7	80
62.50	8	53	47.62	8	20	38.46	8	87
62.02	9	60	47.34	9	27	38.28	9	93
61.54	13.0	8.67	47.06	17.0	11.33	38.10	21.0	14.00
61.07	1	73	46.78	1	40	37.92	1	07
60.61	2	80	46.51	2	46	37.74	2	13
60.15	3	87	46.24	3	53	37.56	3	20
59.70	4	93	45.97	4	60	37.38	4	27
59.26	5	9.00	45.71	5	67	37.21	5	33
58.82	6	07	45.45	6	73	37.04	6	40
58.39	7	13	45.20	7	80	36.87	7	47
57.97	8	20	44.94	8	87	36.70	8	53
57.55	9	27	44.69	9	93	36.53	9	60

¹ Krüger, *Zuckerindustrie-Kalender*, 1910, p. 48.

Table 54.¹

A Table for the Determination of Invert Sugar (G') from the quantity of Sodium Hydroxide equivalent to the Cuprous Oxide obtained in the Estimation of the Reducing Sugar in Cane Juices. (Winter.)

[Note : In order to determine the percentage of invert sugar in a juice, the cuprous oxide is dissolved in 20 c.c. of standard hydrochloric acid, the amount of sodium hydroxide equivalent to the cuprous oxide being found by titration of the excess of acid. In the following Table G' corresponds to the quantity of invert sugar contained in 50 c.c. of the diluted solution. The percentage of invert sugar in the original juice is found by multiplying G' by the factor F (see Table 53), which corresponds to the rotation of the juice. From the column headed "Cu" the percentage of invert sugar may be calculated when the gravimetric method is used.]

Cu.	G'.	NaOH.	Cu.	G'.	NaOH.	Cu.	G'.	NaOH.
...	0·070	0·0269	0·0885	0·110	0·0473	0·1391
...	71	0274	0898	111	0478	1404
...	72	0279	0911	112	0483	1417
...	73	0284	0923	113	0488	1429
...	74	0289	0936	114	0493	1442
0·035	0·0092	0·0443	75	0294	0949	115	0499	1455
36	0097	0455	76	0299	0961	116	0504	1467
37	0102	0468	77	0304	0974	117	0509	1480
38	0107	0481	78	0309	0987	118	0514	1493
39	0112	0493	79	0314	0999	119	0520	1505
0·040	0·0117	0·0506	0·080	0·0319	0·1012	0·120	0·0526	0·1518
41	0122	0519	81	0324	1025	121	0531	1531
42	0127	0531	82	0329	1037	122	0536	1543
43	0132	0544	83	0334	1050	123	0542	1556
44	0137	0557	84	0339	1063	124	0548	1569
45	0142	0569	85	0344	1075	125	0554	1582
46	0147	0582	86	0349	1088	126	0559	1594
47	0152	0594	87	0354	1100	127	0564	1606
48	0157	0607	88	0359	1113	128	0570	1619
49	0162	0620	89	0364	1126	129	0576	1632
0·050	0·0167	0·0632	0·090	0·0370	0·1138	0·130	0·0581	0·1644
51	0172	0645	91	0375	1151	131	0586	1657
52	0177	0658	92	0380	1164	132	0591	1670
53	0182	0670	93	0385	1176	133	0597	1682
54	0187	0683	94	0390	1189	134	0603	1695
55	0192	0696	95	0395	1202	135	0608	1708
56	0197	0708	96	0400	1214	136	0613	1720
57	0202	0721	97	0405	1227	137	0618	1733
58	0207	0734	98	0410	1240	138	0624	1746
59	0212	0746	99	0415	1252	139	0630	1758
0·060	0·0218	0·0759	0·100	0·0421	0·1265	0·140	0·0635	0·1771
61	0223	0772	101	0426	1278	141	0640	1783
62	0228	0784	102	0431	1290	142	0645	1796
63	0233	0797	103	0436	1303	143	0651	1809
64	0238	0810	104	0441	1316	144	0657	1821
65	0243	0822	105	0447	1328	145	0662	1834
66	0248	0835	106	0452	1341	146	0667	1847
67	0253	0847	107	0457	1353	147	0672	1859
68	0258	0860	108	0462	1366	148	0678	1872
69	0263	0873	109	0467	1379	149	0684	1885

¹ Krüger, *Zuckerindustrie Kalender*, 1910, p. 49.

Table 54—*continued.*

Cu.	G'.	NaOH.	Cu	G'.	NaOH.	Cu.	G'.	NaOH.
0·150	0·0689	0·1897	0·200	0·0970	0·2530	0·250	0·1266	0·3162
151	0694	1910	201	0975	2542	251	1271	3175
152	0699	1923	202	0981	2555	252	1277	3188
153	0705	1935	203	0987	2568	253	1283	3200
154	0711	1948	204	0993	2580	254	1289	3213
155	0716	1961	205	0999	2593	255	1295	3226
156	0721	1973	206	1005	2606	256	1300	3238
157	0726	1986	207	1011	2618	257	1306	3251
158	0732	1999	208	1017	2631	258	1312	3264
159	0738	2011	209	1023	2644	259	1318	3276
0·160	0·0744	0·2024	0·210	0·1029	0·2656	0·260	0·1324	0·3289
161	0749	2036	211	1035	2669	261	1329	3301
162	0754	2049	212	1041	2682	262	1335	3314
163	0760	2062	213	1047	2694	263	1341	3327
164	0766	2074	214	1053	2707	264	1347	3339
165	0772	2087	215	1059	2920	265	1353	3352
166	0777	2100	216	1065	2732	266	1358	3365
167	0782	2112	217	1071	2745	267	1364	3377
168	0788	2125	218	1077	2758	268	1370	3390
169	0794	2138	219	1083	2770	269	1376	3403
0·170	0·0800	0·2150	0·220	0·1089	0·2783	0·270	0·1382	0·3415
171	0805	2163	221	1095	2795	271	1387	3428
172	0810	2176	222	1101	2808	272	1393	3441
173	0816	2188	223	1107	2821	273	1399	3453
174	0822	2201	224	1113	2833	274	1405	3466
175	0828	2214	225	1119	2846	275	1411	3479
176	0833	2226	226	1125	2859	276	1416	3491
177	0838	2239	227	1131	2871	277	1422	3504
178	0844	2252	228	1137	2884	278	1428	3516
179	0850	2264	229	1143	2897	279	1434	3529
0·180	0·0856	0·2277	0·230	0·1149	0·2909	0·280	0·1440	0·3542
181	0861	2289	231	1155	2922	281	1445	3554
182	0866	2302	232	1161	2935	282	1451	3567
183	0872	2315	233	1167	2947	283	1457	3580
184	0878	2327	234	1173	2960	284	1463	3592
185	0884	2340	235	1179	2973	285	1469	3605
186	0889	2353	236	1184	2985	286	1474	3618
187	0894	2365	237	1190	2998	287	1480	3630
188	0900	2378	238	1196	3011	288	1486	3643
189	0906	2391	239	1202	3023	289	1492	3656
0·190	0·0912	0·2403	0·240	0·1208	0·3036	0·290	0·1498	0·3668
191	0917	2416	241	1213	3048	291	1503	3681
192	0923	2429	242	1219	3061	292	1509	3694
193	0929	2441	243	1225	3074	293	1515	3706
194	0935	2454	244	1231	3086	294	1521	3719
195	0941	2467	245	1237	3099	295	1527	3732
196	0946	2479	246	1242	3112	296	1532	3744
197	0952	2492	247	1248	3124	297	1538	3757
198	0958	2505	248	1254	3137	298	1544	3769
199	0964	2517	249	1260	3150	299	1550	3782

feeding-stuffs (so-called "molas-cuit") no reliable methods are at present known. The most satisfactory analytical procedure is the following, due to Prinsen-Geerligs.¹ A weighed portion of the material is thoroughly extracted with water, the extract made up to a definite volume, and the Brix value, the rotatory power after inversion, and the reducing sugar estimated. The sum of the cane and invert sugar gives the total sugar present from which the purity of the molasses, the proportion present, and the sugar and molasses content of the feeding-stuff can be calculated, on the assumption (based on experience) that cane molasses contain on an average 60 per cent. of total sugar.

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¹ *Archiv für die Zuckerindustrie Javas*, 1909, 17, 601.

STARCH AND DEXTRIN

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I. STARCH.

THE manufacture of starch depends mainly on very simple mechanical operations, which consist in grinding the raw material finely, in order to disintegrate the starch-containing cells, from which the starch is washed out with water, allowed to settle, and dried.

In cases in which the contents of the cells cannot be sufficiently disintegrated for washing out the starch, as with the cereals, the raw material is either allowed to undergo fermentation or it is submitted to the action of chemicals, such as caustic alkalis and acids, particularly sulphurous acid.

In practice a regular analytical control of the factory working is not exercised, although this is much to be desired. It is generally considered sufficient to examine the raw materials for their content of starch, and the final product for its commercial purity and content of water.

The analytical methods of examination concerned with starch and its manufacture relate, 1. to the raw material; 2. to the manufactured product; 3. to the waste products; 4. to the auxiliary raw materials used in the manufacture.

A.—THE EXAMINATION OF RAW MATERIALS.

The analysis of all raw materials for the purpose of manufacture is usually limited to an estimation of the starch. In the case of grain, the estimation of the content of water is also carried out, and with wheat, that of nitrogenous substances.

The estimation of starch is effected either by simply washing out, or by chemical means; also (in the case of potatoes), by taking the specific gravity.

1. Estimation of Starch by Washing out the Raw Material.

A weighed quantity of the raw material to be analysed is steeped in water, mashed and washed, as on the large scale, either over a fine meshed sieve or tied up in bolting cloth and washed until the washings run off clear. Flour is kneaded to dough; potatoes are reduced to a fine state of division. The starch readily settles out from the wash-water, and is then repeatedly washed by decantation, placed in a dish, dried, and weighed.

In order to estimate directly the yield of starch from potatoes, Günther¹ constructed an apparatus in which a weighed quantity of potato (250 g.) is pulverised and washed by means of a grinding roller. The water, containing the starch in suspension, flows into a measuring cylinder, in which it is allowed to remain for six hours. By this time the starch will have settled out, and by reading the cylinder an estimate may be arrived at of the percentage of primary, secondary, and sludge starch obtainable from the potatoes under examination.²

It will be obvious that this method gives only an approximate idea of the percentage of starch. For instance, in potatoes containing 21 per cent. of starch, only 14-15 per cent. is found; the residue remains on the sieve in the cells unbroken through incomplete maceration.

2. Estimation of Starch by Chemical Analysis.

The chemical methods for the estimation of starch in raw materials can be carried out either by direct or by indirect means. In the latter case the starch is either converted into dextrose or into maltose and dextrin, the cupric reducing power being estimated and the percentage of starch calculated from the result.

Of the indirect methods for the estimation of starch, the most commonly adopted are Reinke's method, in which the starch is converted into the soluble form by stirring up the substance with water, adding lactic acid and applying a high pressure; and Märcker and Morgan's method, which depends upon the fact that the finely ground cereals or dried potato for analysis are gelatinised by boiling with water, and the starch brought into solution by the addition of malt extract. Both methods are combined in the method of Lintner,³ in which the extraction of the starch is brought about by means of malt diastase with the subsequent application of high pressure.

The starch dissolved and partially hydrolysed by one or other of the above methods is further hydrolysed with hydrochloric acid, and the sugar formed estimated by the cupric reduction method. These

¹ *Z. Spiritusind.*, 1884, p. 93.

² Potato starch is known in commerce as farina.

³ *Z. angew. Chem.*, 1898, **11**, 725.

methods are described in the section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., pp. 688 *et seq.*

In England a method for the estimation of starch was devised by C. O'Sullivan¹ in 1884. It depends on extracting the finely divided grain first with ether to remove the fat and then with alcohol of sp. gr. 0.900 at about 35° to remove certain gums, the removal of which is completed by washing with water at the same temperature. The residual starch is then boiled with water and the paste digested for an hour at 62°-63° with a little diastase. The maltose and dextrin are then estimated in the filtrate from the polarimetric reading and the cupric reducing power, the specific gravity of the liquid, corrected for the diastase, being employed as a check. From the amount of hydrolysed products so determined, the original amount of starch which gave rise to them is readily calculated. H. T. Brown and his colleagues² have investigated the method, and have shown that with certain modifications it can be used for the estimation of starch in barley and malt.

The fact has been ignored, however, by both O'Sullivan and Brown that barley and malt contain insoluble pentosans which, as observed by Lintner,³ are dissolved and hydrolysed by malt enzymes; consequently the presence of these hydrolysed pentosans will vitiate the accuracy of the method, and the results must be corrected for the reducing power due to them. The method is very tedious and lengthy.

In order to arrive at the content of starch by any of these indirect methods, the quantity of ready-formed sugars and pentosans must be estimated separately and the first result corrected. The sugar estimation appears important in the case of potatoes, since these exhibit a very varying content of sugar according to their maturity, conditions of storing and species, which amounts, according to the observations of Saare, to 4 per cent.

Estimation of Sugar in Potatoes.—Saare⁴ gives the following method for this estimation:—1000 g. of potatoes are mashed in the usual kitchen cullender, the pulp put into a straining cloth, squeezed out in the ordinary hand press, and the resulting juice filtered; 200 g. of the filtrate are mixed with 1 c.c of *N*/1 sulphuric acid (= 0.04 g. SO₃), heated to boiling once (in order to kill bacteria), cooled and allowed to ferment with 2 g. of pure yeast or pressed yeast at room temperature. After the action has ceased (seventeen to eighteen hours), about 100 g. of the total contents of the fermenting flask is distilled, diluted to 100 g. and the content of alcohol estimated, either by the pyknometer or by an alcohol hydrometer. If, *e.g.*, 200 g. of potato juice give 100 g. of

¹ *J. Chem. Soc.*, 1884, 45, 1.

² *Trans. Guinness Research Laboratory*, 1903, vol. i, part i, p. 79.

³ *Z. angew. Chem.*, 1898, 11, 726.

⁴ *Fabrikation der Kartoffelstärke*, 1897, p. 489.

distillate of sp. gr. 0.9946 at 15°, then 100 g. = 2.94 g. of alcohol,¹ or 100 g. of juice yields 1.47 g. of alcohol. If, now, 100 g. of dextrose yields theoretically 48.67 g. of alcohol (according to Jodelbaur), it follows that 1 g. of alcohol = 2.055 g. of dextrose; therefore 1.47 g. of alcohol = 3.02 g. of dextrose in 100 g. of juice.

In order to estimate sugar (expressed as dextrose) in potatoes, the quantity of dry substance in the juice and in the potato must be known.

Estimation of the Total Solids of Potatoes.—For this purpose 1000 g. of the well-mashed and re-dried sample is cut up with a cucumber-slicer, avoiding loss, into slices and dried. The drying takes place very quickly if the slices are spread out in a very large porcelain dish, so as to cover each other as little as possible, and the dish heated on a large iron water-bath; after about twelve to twenty hours, the slices are sufficiently hard to powder. They are then allowed to stand several hours (*e.g.*, overnight) in the air, and weighed. This gives the air-dried residue, *e.g.*, = 279.28 = 27.92 per cent. It is quickly ground in a hand mill, and a portion (about 10 g.) weighed out into a covered metal crucible or weighing tube and heated for four hours at 105° in an air-oven, cooled in a desiccator, and weighed. If, for instance, 9.6070 g. of air-dried substance = 8.7770 g. of residue, then the air-dried substance contains $\frac{8.777 \times 100}{9.607} = 91.36$ per cent. of anhydrous substance, and the original potatoes $\frac{27.92 \times 91.36}{100} = 25.51$ per cent. of anhydrous substance, and the content of water is accordingly 74.49 per cent.

In order to estimate the dry matter in potato juice, about 10 g. of the juice are weighed off into a weighing-bottle and dried to constant weight at 105°. If 10.1105 g. of juice give 0.5925 g. of residue, then the juice contains 5.86 per cent. of dry matter, or 94.14 g. of water.

To this belong 3.02 g. of sugar (dextrose). If 100 g. of potato contained 25.51 g. of dry matter or 74.49 g. of water, therefore there corresponds to this in the juice $\frac{74.49 \times 3.02}{94.14}$ g. = 2.39 g. of sugar. The potatoes therefore contain 2.39 per cent. of sugar (dextrose).

The Pentosans are estimated by the phloroglucide method of Tollens. The determination, which depends on the conversion of the pentosans and pentoses into furfural by means of hydrochloric acid and precipitation with phloroglucinol, is carried out according to Lintner as follows:—

A flask of 250-350 c.c. capacity is placed in a small iron dish containing a layer of Rose's metal 1 cm. deep. The flask is provided

¹ A Table for ascertaining the content of alcohol in mixtures of alcohol and water is given in the section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., p. 711.

with a double-bored rubber stopper, through one of the holes of which passes a pipette of about 50 c.c. capacity provided with a stopcock and reaching 4 cm. into the neck of the flask. A wide distillation tube, fitted with a bulb, passes through the other hole and is attached to a condenser. A glass beaker marked for 30 c.c. is placed under this as a receiver. From 3-6 g. of the sample is heated with 100 c.c. of hydrochloric acid of sp. gr. 1.06 (12 per cent.) in the metal bath, so that 30 c.c. distil over in ten to fifteen minutes. The beaker is then replaced by another, an additional 30 c.c. of hydrochloric acid added to the flask through the tapped pipette, and a further 30 c.c. distilled over, etc. The distillates are filtered through a small filter, to remove the fat which has been carried over, and are collected in a beaker with a mark at 400 c.c. The distillation is carried on until 1 drop of the distillate no longer gives a red colour on paper soaked in aniline and glacial acetic acid (9:6). A quantity of phloroglucinol (for grains 0.3 g.), dissolved in a few cubic centimetres of hydrochloric acid equal to double the amount of furfural expected, is then added to the total filtrate and the latter made up to 400 c.c. with hydrochloric acid of sp. gr. 1.06. The black precipitate (phloroglucide) is allowed to settle until the next day; it is then collected on a tared filter paper, washed with 150 c.c. of water, dried for three hours at 105°, and weighed.

Parow has simplified the method by allowing the hydrochloric acid to drop from the tap-pipette at the same rate as it distils over, and by arranging for a continuous filtration of the distillate through a small filter into the 400 c.c. beaker. The end reaction is carried out in a porcelain dish, in which a drop each of the distillate, aniline, and glacial acetic acid are placed.

In order to obtain concordant results, it is necessary to estimate approximately the amount of pentosans by a preliminary experiment, and to use no more of the substance than corresponds to 0.25 g. of pentosans, *e.g.*, in potato containing 3-4 per cent. of pentosans about 6 g.

To calculate the furfural, the weight of phloroglucide obtained is divided by a number which varies between 1.82-1.92 for 0.2-0.4 g. of phloroglucide respectively. The weight of furfural is multiplied by 1.84 to give the corresponding weight of the pentosans.

The following Table for the direct conversion of phloroglucide to pentosan has been published by Kröber¹ :—

Phloroglucide.	Pentosan.	Phloroglucide.	Pentosan.	Phloroglucide.	Pentosan.
0.100 =	0.0935	0.170 =	0.1554	0.240 =	0.2168
0.110 =	0.1023	0.180 =	0.1642	0.250 =	0.2256
0.120 =	0.1111	0.190 =	0.1729	0.260 =	0.2343
0.130 =	0.1201	0.200 =	0.1817	0.270 =	0.2429
0.140 =	0.1288	0.210 =	0.1904	0.280 =	0.2517
0.150 =	0.1377	0.220 =	0.1992	0.290 =	0.2605
0.160 =	0.1465	0.230 =	0.2081	0.300 =	0.2693

¹ *J. für Landwirtschaft*, 1900, 48, 357.

A method for the estimation of furfural, described by J. T. Flohil,¹ depends on the reducing action of furfural towards Fehling's solution. The method is carried out as follows:—50 c.c. of the acid distillate (the total quantity of which amounts to 400 c.c.) is neutralised, treated with 20 c.c. of Fehling's solution, and made up to 100 c.c., the whole being boiled for thirty-five minutes under a reflux condenser. In order to avoid any loss of furfural a few pieces of ice are placed in the upper end of the condenser tube, which is funnel-shaped. According to Flohil, a blank determination must be made in which the same quantity of sodium chloride is present. Flohil found that under these conditions the furfural:copper ratio is 0.3775:1, *i.e.*, 1 mol. of furfural is equivalent to 4 atoms of copper or 2 atoms of oxygen. The amount of cuprous oxide may be found not only by direct weighing but indirectly by the determination of the unreduced copper iodometrically; Schoorl's² method is employed for this purpose.

This method has been investigated by L. Eynon and J. H. Lane,³ who find that the copper-reducing power of furfural is not independent of the concentration, the furfural:copper ratio ranging from 0.376-0.450 as the amount of furfural present is increased from 0.01-0.05 g. There is therefore no ground for Flohil's assumption of a simple relation between the weights of furfural and the copper. It was found to be unnecessary to use ice in the top of the condenser tube as recommended by Flohil; further, it was shown that the presence of sodium chloride does not affect the reducing power of furfural, so that it is not necessary to carry out a blank experiment as stated by Flohil.

Eynon and Lane's results are epitomised in the following Table:—

Weight of furfural.	Weight of cuprous oxide (corrected).	Weight of copper (corrected).	Ratio $\frac{\text{Furfural}}{\text{copper.}}$
g.	mg.	mg.	mg.
0.0100	30.0	26.6	0.376
0.0200	57.0	50.6	0.395
0.0300	81.0	71.9	0.417
0.0400	103.5	91.9	0.435
0.0500	125.0	111.0	0.450

It will be seen that, even as revised by Eynon and Lane, the method is inferior in accuracy to the phloroglucide method.

A method has been worked out by G. Baumert and H. Bode⁴ for estimating the starch in potatoes, which depends on the fact that starch is readily soluble in aqueous potassium hydroxide, and can be precipitated quantitatively by the addition of alcohol to this solution. This method is carried out in the following manner:—3 g. of very finely ground air-dried potatoes is mixed in a porcelain beaker with about

¹ *Chem. Weekblad*, 1910, 7, 1057.

² *Z. angew. Chem.*, 1899, 12, 633.

³ *Analyst*, 1912, 37, 41.

⁴ *Z. angew. Chem.*, 1900, 13, 1074 and 1111.

50 c.c. of cold water. After the mixture has been allowed to stand for one hour, with occasional stirring, the liquid is decanted (to remove sugar, etc.) from the deposited substance through a small asbestos filter (sieve-plate 2-3 cm. diameter) as completely as possible, the asbestos filter with its contents returned to the beaker, 50 c.c. of water again added, and the beaker closed with a cover and heated in a Soxhlet digester for three and a half hours at approximately (not above) 3 atmos. pressure. After cooling, the contents of the beaker, mixed with 150-200 c.c. of boiling water, are transferred to a 250 c.c. graduated flask and boiled for ten minutes in order to dissolve the starch completely. After again cooling, the flask is filled up to the mark at 15°, the contents well mixed and filtered through a pleated filter paper. 100 c.c. of the filtrate is then mixed with 10 c.c. of a 10 per cent. solution of sodium hydroxide, whereby the opalescence of the liquid disappears and a permanently clear solution results. 25 c.c. of this solution is mixed whilst stirring with about 100 c.c. of 94-96 per cent. alcohol, about 1 g. of fine flocculent asbestos added before the precipitate has time to agglutinate, and the whole vigorously stirred until the precipitate settles rapidly, while the liquid becomes clear. If this does not take place in about one minute, further small quantities of asbestos are added with continuous stirring until the settling is complete.

As in the dextrose estimation, the solution is filtered, with careful suction, through a previously ignited Soxhlet's asbestos filter-tube, the clear liquid being first poured on; then the precipitate, without compressing it with the glass rod, is stirred with 80 per cent. alcohol, and so in a cautious manner brought on to the filter as deflocculated as possible, and washed. During the washing, care must be taken that the tube always contains liquid. The most suitable way of removing the last traces of the precipitate from the beaker is to wash this out, using a suitably trimmed feather, with the hydrochloric acid required for the decomposition of the starch sodium compound amounting to 3-5 c.c. of 5 per cent. hydrochloric acid. The dissolved substance is again precipitated with 25-30 c.c. of 94-96 per cent. alcohol, the precipitate transferred to the filter and washed, first with 80 per cent. alcohol, then with absolute alcohol, and finally with anhydrous ether. After the ether has been completely removed by suction, the filter is dried to constant weight in a current of air (in an air- or sand-bath) at 120°-130°, and after cooling in the desiccator is weighed. A current of air or oxygen is then passed through the tube, which is heated carefully by a gas flame in the direction of the current. The starch is thus quickly burnt, without leaving behind any residue of charcoal, at so low a temperature that the asbestos scarcely glows.

The tube is then allowed to cool in the desiccator, and by weighing,

the loss due to ignition obtained. This is equivalent to the amount of starch contained in 25 c.c. of the original starch mixed with the sodium hydroxide solution, and equal to the amount of starch present in 0.3 g. of air-dried substance, if it is increased by $\frac{1}{10}$, corresponding to the dilution of the solution due to the addition of the sodium hydroxide. If the weight of the fresh potato is denoted by f , that of the air-dried substance obtained from this by l , and the loss in weight due to ignition of the asbestos tube by v , then the percentage content of starch in the fresh material may be calculated from the formula:—

$$S = \frac{100 (v \times 1.1)}{0.3} \cdot \frac{l}{f}$$

Behrend and Wolfs¹ obtained very accurate results with this method, in the analysis of potatoes, but too low results in the case of wheat and maize. They recommend somewhat wider tubes for filtering (with 20-22 mm. internal diameter), and the burning off of the starch in a current of oxygen.

According to H. Witte,² who modified the method of Baumert and Bode for the analysis of wheat flour and commercial starch, 1 g. of substance and two hours' heating at 4 atmos. pressure is sufficient for wheat-flour.

Baumert³ has more recently considerably simplified his method by using fuming hydrochloric acid, as suggested by C. J. Lintner, for the disintegration of the substance or solution of the starch. This modification is applicable to all starches (wheat, rye, barley, oats, rice, maize). The details of analysis are as follows:—3 g. of the substance in the finest possible powder is evenly macerated in a beaker with 2.5 c.c. of water, and mixed with 10 c.c. of hydrochloric acid (sp. gr. 1.19) with continual stirring and cooling (by placing in cold water). To the gelatinous mass, which will have become fluid in ten minutes at most, an excess of sodium hydroxide (20 per cent.) is added, the mixture being well stirred and cooled. The contents of the beaker are then washed with water into a 250 c.c. flask, made up to the mark, well shaken, and, after allowing to settle, filtered through a pleated filter paper. 25 c.c. of the filtrate, after the addition of about 1 g. of finely flocculated asbestos, is precipitated with 50-60 c.c. of alcohol (94-96 per cent.), whilst being vigorously stirred. As soon as the precipitate has quite settled, it is collected by the aid of suction on a previously ignited asbestos filter-tube, washed with alcohol with the addition of 3-5 c.c. of dilute hydrochloric acid (to decompose the sodium starch compound), then with 80 per cent. alcohol, again

¹ *Z. angew. Chem.*, 1901, 14, 461.

² *Ibid.*, 1904, 17, 65.

³ *Z. Unters. Nahr. u. Genussm.*, 1909, 18, 167.

with absolute alcohol, and finally with ether. After the tube has been dried and weighed, the contents are heated in a current of oxygen, and the tube re-weighed after cooling. The loss in weight is calculated as starch.

The following methods used by Lindet and von Kaiser are also suitable for the direct estimation of starches.

In order to dissolve the gluten which surrounds the starch grains in a solid network, Lindet¹ allowed a hydrochloric solution of pepsin to act on the ground grain. The starch flour is thus freed from the gluten, and can then be removed mechanically from the remaining parts. The *modus operandi* is as follows:—About 10 g. of corn is ground, placed in an Erlenmeyer flask with a solution containing 2 per cent. pepsin and 1.5 per cent. hydrochloric acid, and maintained for twelve to twenty-four hours at a temperature of 40°-50° with an occasional thorough shaking. The residue is then wrapped in a silk bag, and thoroughly kneaded in a dish with water, until no more starch meal is obtained. This is then caused to settle by the addition of formaldehyde, collected on a filter containing a weighed quantity of washed and calcined pumice-stone, and dried with this, first at 50° and then at 105°. The method permits of the estimation of starch in presence of much sugar.

Kaiser's method,² which depends on the complete precipitation of gelatinous starch by iodine in presence of sodium acetate, is carried out as follows:—50 c.c. of a 1 per cent. starch solution obtained by gelatinising and cooling is mixed with 10 g. of sodium acetate, warmed to 50°, and precipitated whilst stirring with 25 c.c. of iodine solution (5 g. I and 10 g. KI in 1 litre), so that a small excess of iodine is present. The precipitate is collected on a tared filter, washed with a 3 per cent. solution of sodium acetate, then washed out with alcohol into a porcelain dish, mixed with about 5 c.c. of a 5 per cent. alcoholic solution of potassium hydroxide, and gently warmed, when amorphous starch remains as a residue. This is then acidified with sufficient alcoholic acetic acid, allowed to stand for a time to remove all alkali, and the precipitate returned to the weighed filter, washed eight times with hot 90 per cent. alcohol, then with absolute alcohol and ether successively, and dried for four hours at 120°. The starch should be almost completely soluble in water; any residue is to be deducted after drying. Since starch is very hygroscopic, it must be weighed in a closed vessel.

¹ Märcker-Delbrück, "Spiritusfabrikation"; *Woch. f. Brau.*, 1896, p. 1302.

² Märcker-Delbrück, "Spiritusfabrikation"; *Chem. Zeit.*, 1902, 26, 180.

3. Polarimetric Estimation of Starch.

This method was originally proposed by Dubrunfaut. C. J. Lintner's¹ modification, which was devised for the estimation of starch in barley, is carried out as follows:—5 g. of barley, ground as fine as possible, are triturated in a mortar with 20 c.c. of water to avoid the formation of lumps, and mixed with 40 c.c. of concentrated hydrochloric acid² (sp. gr. 1.19); the mixture is allowed to stand for thirty minutes, when the initial clear yellow-coloured pulp becomes darker and more fluid. The liquid is then washed out with hydrochloric acid of sp. gr. 1.125, and transferred with the help of a rubber-covered glass rod into a 200 c.c. flask, 10 c.c. of a 4 per cent. solution of phosphotungstic acid added (for defecating), and the whole made up to the mark with dilute hydrochloric acid. After vigorous shaking, the solution is filtered through a pleated filter paper, the point of which is suitably protected by a small, smooth filter, and the rotation of the perfectly clear filtrate determined in a 200 mm. tube, in an instrument employing sodium light. Instead of 5 g. of barley, 2.5 g. of the sample may be used, by keeping to the corresponding proportions of reagents, viz.: 10 c.c. of water, 15 c.c. of concentrated hydrochloric acid, and using a 100 c.c. flask. The results are calculated by a formula assuming the specific rotatory power of the dissolved starch is $[\alpha]_D^{20} 200^\circ.3$.

O. Wenglein³ has pointed out that the acid fumes resulting from the use of concentrated hydrochloric acid in Lintner's method are objectionable, and has proposed the following modification, in which sulphuric acid is used in place of hydrochloric:—2.5 g. of the barley meal is triturated with 10 c.c. of distilled water, and 20 c.c. of sulphuric acid (sp. gr. 1.70) are added with stirring. After ten to fifteen minutes, the solution is rinsed into a 100 c.c. flask with sulphuric acid of sp. gr. 1.30 and 5 c.c. of 4 per cent. phosphotungstic acid. The solution is then made up to 100 c.c. with sulphuric acid of sp. gr. 1.30, mixed, filtered, and its rotation observed in a 200 mm. tube. The specific rotatory power of barley starch dissolved by this method is found to be $[\alpha]_D^{19} 191^\circ.7$.

L. T. Thorne and E. H. Jeffers⁴ have drawn attention to the main sources of error in such methods as those of Lintner. There are, they state, the risk of too advanced hydrolysis if the acid is too concentrated, or the temperature too high, and the risk of imperfect extraction or of partial re-precipitation if the acid is too dilute at any period of the operation. They find the following modification of Lintner's method

¹ *Z. ges. Brauw.*, 1907, 30, 109.

² In a subsequent paper (*Woch. f. Brau.*, 1909, 26, 306) Lintner has reduced the amount of hydrochloric acid of sp. gr. 1.19 to 30 c.c.

³ *Z. ges. Brauw.*, 1908, 31, 53.

⁴ *Proc. 7th Internat. Congress of Applied Chemistry*, sect. vi., A., p. 14.

to give the best results:—5 g. of the material, previously reduced to a finely divided state, is triturated with about 20 c.c. of water to a smooth cream, hydrochloric acid of sp. gr. 1.15 then added, with continued trituration, in portions of about 5 c.c. at a time until the mass first swells up into a jelly and finally breaks down into a viscous liquid. This requires about twice as much acid as the water first used, unless the original material contained much moisture, when the quantity of acid required is somewhat greater. The mixture is allowed to stand for about ten minutes and is then transferred to a 200 c.c. flask, into which has been previously measured 10 c.c. of a 4 per cent. solution of phosphotungstic acid and 20 c.c. of hydrochloric acid of sp. gr. 1.15. The mortar is rinsed with dilute hydrochloric acid (sp. gr. 1.1) and the whole made up to 200 c.c. with dilute hydrochloric acid (sp. gr. 1.1). After mixing, the contents of the flask are transferred to a wide-necked stoppered bottle and thoroughly shaken (or placed in a centrifugal machine) till a well-defined flocculent precipitate is obtained and the supernatant liquid is fairly bright. The rotation of the filtrate is taken in a 200 mm. tube by means of a Schmidt and Haensch quartz compensating polarimeter. The percentage of starch is calculated by means of the formula,

$$S = \frac{R \times 40}{11.6}$$

in which R = the reading in Ventzke divisions.

A. Schall¹ found that the clarification of the solutions was very variable and often very imperfect if Lintner's method was applied directly to potatoes. According to his experiments the clarification can be omitted, if the weighed potato pulp is brought on to a starch-proof asbestos filter and freed from soluble matter by suction and washing with water. For a filter-plate of 5 mm. diameter, 0.6 g. of asbestos is sufficient. The very small error due to this (with asbestos of a sp. gr. of 3.0 = 0.2 c.c.) may easily be corrected by using a weighed amount of asbestos. A correction has to be made also in exact determinations for the cellulose insoluble in hydrochloric acid. The average volume of this insoluble matter, as a result of many experiments, was fixed at 0.38 c.c. for 10 g. of potatoes. The total correction, therefore, for 20 g. would amount to 0.76 c.c. The following was found by Schall to be the most suitable way of carrying out the method:—20 g. of the well-mixed homogeneous potato pulp is run on to a perforated plate provided with an asbestos layer capable of retaining the starch, and the liquid portion sucked off with the aid of a pump. The residue is washed three times with 5-10 c.c. of water, three times with about 5 c.c. of 96 per cent. alcohol, and finally with a little ether. The residue,

¹ *Z. Unters. Nahr. u. Genussm.*, 1909, 18, 157.

together with the asbestos, is then returned to the dish used for weighing the pulp, mixed with 20 c.c. of water, 40 c.c. of concentrated hydrochloric acid (sp. gr. 1.19) added, and the mass rendered as uniform as possible by stirring. After standing for about a quarter of an hour, it is again well mixed, allowed to stand for a further fifteen minutes, and the pulp then washed out with water into a 200 c.c. flask and made up to the mark with water. A correction should be made for the volume of the suspended matter, which may be taken as 0.9 c.c. The rotation of the filtrate is taken at the normal temperature.

The latest method of E. Ewers¹ is carried out as follows:—5 g. of the finely divided substance are poured into a 100 c.c. flask with 25 c.c. of dilute hydrochloric acid, containing 1.125 per cent. by weight of hydrogen chloride in the case of cereals and cereal starches, and 0.422 per cent. for potato and arrowroot starches, and the residue washed into the flask with a further 25 c.c. of hydrochloric acid. The flask is placed in a boiling water-bath for exactly fifteen minutes, being repeatedly shaken during the first three minutes. After heating, the solution is made up to 90 c.c., cooled to 20° and defecated with 2 c.c. of sodium molybdate solution (prepared by fusing 30 g. of molybdic acid with 25 g. of anhydrous sodium carbonate, dissolving the product in water to 250 c.c., and filtering), or with 10 c.c. of 4 per cent. phosphotungstic acid, made up with water to 100 c.c., mixed, filtered and the rotatory power of the filtrate determined at 20° in a 200 mm. tube, using a Schmidt and Haensch half-shadow, quartz compensating polarimeter. The observed reading in Ventzke divisions multiplied by the factor 1.912 gives in the case of barley the percentage of starch, the specific rotatory power of the matter dissolved from barley starch under these conditions being according to Ewers,² $[\alpha]_D 181^\circ.5$.

Note by Arthur R. Ling.—As a result of much practical experience during recent years in the estimation of starch in various products, Ewers's method has been found to be preferable to any other as being cleaner and giving more constant results. With certain products, however, the results may be vitiated by the presence of optically active substances other than starch derivatives. This applies, however, equally to all polarimetric methods of estimating starch.

4. Estimation of Starch in Potatoes by the Specific Gravity Methods.

These methods, which depend on the fact that of the solid organic constituents of potatoes starch is the one of highest specific gravity, have been worked out in Germany for purposes of works' control. The limit of accuracy is about 1 per cent., and, further, it must be

¹ *Zeits. öffentl. Chem.*, 1908, 14, 8, 150.

² *Z. ges. Brauw.*, 1908, 31, 250.

pointed out that the other carbohydrates in the potato, as well as to a certain extent the mineral constituents, are included with the starch. The principle was first employed by Berg, and the method developed later by Lüdersdorff, Balling, and Holdefleiss, whilst it was further worked out by Märcker, Behrend, and Morgan. One of these methods, viz., that devised by Slohmann, depends on measuring the volume of water displaced by 1000 g. of potatoes. The methods most commonly adopted, however, consist in determining the volume of water displaced by 5000 g. of potatoes (weighed in air) from the loss in weight when they are again weighed under water, and many arrangements have been devised for this purpose.

An exhaustive description of these methods is given in the German edition of this work (Vol. IV., pp. 125 *et seq.*). Since, however, potatoes are not grown in Great Britain for starch manufacture, it is superfluous to reproduce this description in the English edition.

B.—THE EXAMINATION OF DIFFERENT STARCHES.

As starch has always the same chemical composition, no matter from what material it may have been obtained, its origin cannot be proved by chemical analysis. Residues of the raw materials used frequently, however, occur in commercial starch, the nature of which may be established by chemical reactions, so that the kind of starch under examination may be deduced in this way. These reactions are little used in the testing of starch; they serve rather for the analysis of flour, but are not always reliable.

Of the two methods which are in general use, that due to Böttger,¹ according to which starch containing gluten can be recognised in presence of starch free from gluten (potato starch, arrowroot), is carried out as follows:—1 g. of starch is heated to boiling with 180 c.c. of water, the paste being vigorously stirred round with a glass rod. If the starch contains gluten, even the smallest trace, a froth is formed which is permanent even after the boiling ceases; if gluten is absent, the froth disappears as soon as the boiling slackens. The presence of gluten can also be proved by a nitrogen determination.

The second analytical method relates to the determination of arrowroot in presence of potato starch. 1 part of starch with 10 parts of a mixture of 2 parts of hydrochloric acid and 1 part of water are shaken for ten minutes. If arrowroot is present, the starch is completely deposited; in presence of potato starch, a jelly-like mass is formed with an odour of fresh beans.

The only sure method of detecting the various kinds of starch is by examining them under the microscope. It is possible to distinguish

¹ *Pol. Notizbl.*, 1869, p. 15.

between the different starches, with some practice, by means of their characteristic shape and the distinctive sizes of the granules of individual starches. While, for a more thorough study of the microscopical character of the several kinds of starch, reference must be made to Nageli's *Die Stärkekörner*, J. Wiesner's *Technische Mikroskopie*, to the work on starch by A. Tschirch in the *Real-Enzyklopädie, der gesamten Pharmazie*, and to A. Meyer's monograph, *Untersuchungen über die Stärkekörner*, illustrations of the most commonly occurring starches are appended (after J. Wiesner from Märcker's *Handbuch der Spiritusfabrikation*).

1. *Potato Starch*.—The starch granules of potato are egg-shaped, of circular cross-section, and often of regular structure; only the young undeveloped granules, as yet possessing no striations, are spherical. The hilum is eccentric and always situated near the small end of the granule. The eccentric striæ are also numerous, and usually distinctly marked; some of them always stand out with remarkable sharpness (Fig. 72).

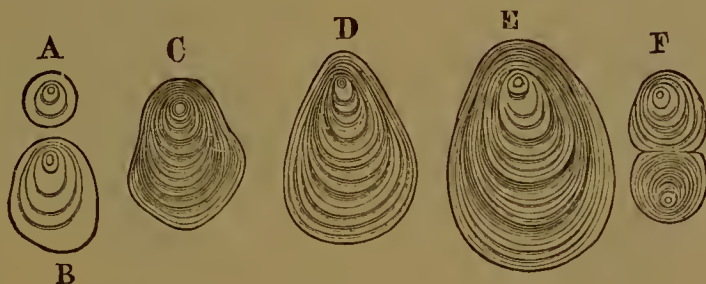


FIG. 72.

Magnified 300 times. Potato starch: A-E simple starch granule; A young undeveloped granule; B-E developed granules; F compound granules.

2. The starch granules of *Rye, Wheat, and Barley* show such a great similarity one to another that they can only be distinguished by the most careful microscopical measurement; on the other hand, they have in common such a strongly characteristic mark that they may be with ease distinguished from all other starches. The granules are of two sizes; large and small granules are found, without any of medium size. The large granules are lenticular, the small ones of spherical, sometimes of polyhedral form. They either show no striæ at all, or only a few striations, and a hilum is seldom directly visible; the situation of the hilum is, however, frequently indicated by one or more faintly marked cracks. The small granules always appear unstriated; in place of the hilum there is usually an air hole (Fig. 73).

In order to distinguish between the three kinds of starch of this group, Wiesner states that the small starch granules of barley lying in water show almost throughout Brownian motion; with those of wheat, on the other hand, only a few, *i.e.*, those approximating to the

minimum 0.0022 mm., show this characteristic. In wheat and rye starches there are approximately equal quantities of small granules for a given quantity of larger ones; in barley starch, the quantity of small granules are relatively larger. Wiesner, however, gives no figures.

3. *Oat Starch* consists partly of compound granules; in the majority of cases 20-70 compound granules (according to Nägeli even up to 300) are bound to one ellipsoidal conglomerate. Each separate starch granule is polyhedral, usually irregularly tri-hexahedral. The single granules are quite distinct from the fragmentary granules; they

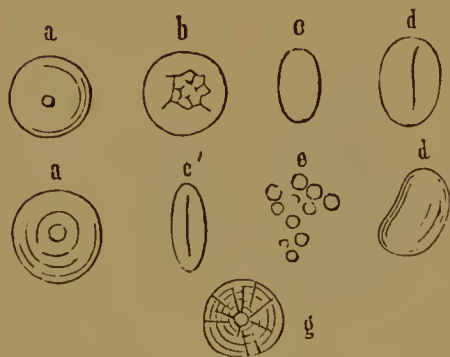


FIG. 73.

Magnified 300 times. Wheat starch; *a-d* large, *e* small granules; *ab* surface view, *cc'* side view of granule; *b* granule with reticulated impression, originating from the small granules. *c'* *d'* granules with cleavages formed by cracks passing through the hilum.

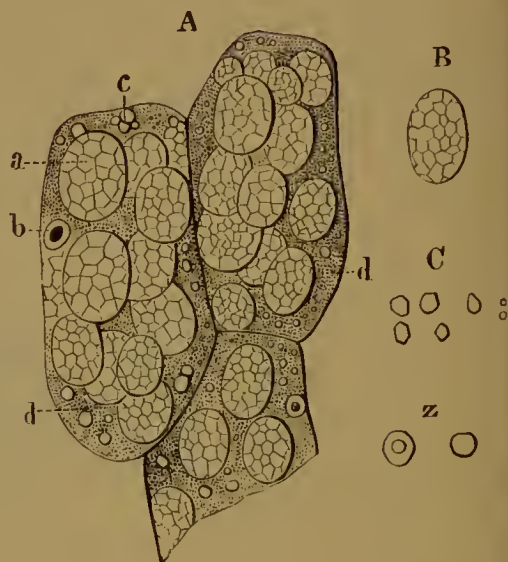


FIG. 74.

Magnified 300 times. A a starch-containing cell from the albuminous part of an oat seed, *a* natural compound starch granule, *bc* simple starch granule, *e* protoplasm residue. B compound granule. C fragmentary granule. Z simple granule. C and Z rather more strongly magnified.

have a round or barrel-shaped appearance, never polyhedral, since they are never fractured granules (Fig. 74).

4. *Rice Starch* consists likewise of compound and single granules (Fig. 75). The compound granules are composed of 2-100 fragmentary granules. Each fragmentary granule is polyhedral, usually penta- or hexahedral, sometimes trihedral and has in place of the hilum a large polygonal, frequently stellate cavity. The single starch granule of rice starch cannot be distinguished from the fragmentary granules of compound granules. The single granules lie thickly crowded together in the cells, filling up the space set free by the compound granules, and thus form pseudo-compound granule groups, which on breaking up yield fractured granules.

5. Starch granules of *Maize* are of three kinds—single, compound,

and fractured granules. In the extreme horny part of maize corn, the granules lie thickly crowded together, united as pseudo-granules. In the inner floury part, the majority of the granules are single; some few are typically compound and consist then of 2-7 fragmentary granules. The single granules are round and indeed spherical or ellipsoidal; the fractured and compound granules, on the other hand, are plain with rounded, polyhedral angles; otherwise all the granules agree in construction. The majority of starch granules exhibit a hilum; the dry ones are penetrated with radial fissures proceeding from the hilum. Striæ are only seen occasionally in the unchanged

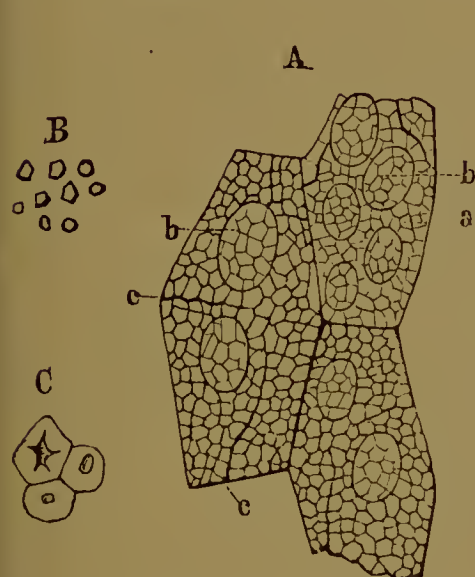


FIG. 75.

A and B magnified 300 times. A cells from rice starch. *a* not originally compound starch, *b* once compound starch granules, *c* cracks produced by drying of the tissue. B single granules of *a* and *b*. C the same more strongly magnified.

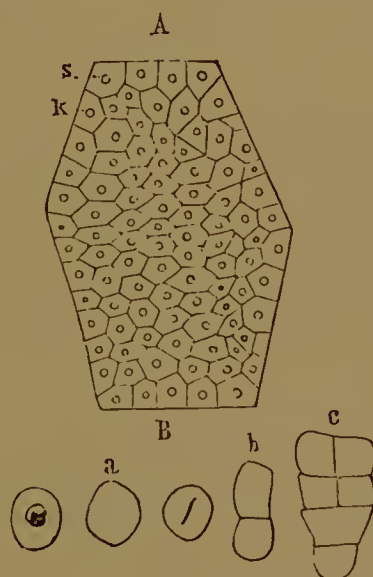


FIG. 76.

Magnified 300 times. A starch-containing cell from the horny part of maize grain. *s* single starch granule, *k* hilum. B *a* simple, *b* and *c* original compound starch granules from the floury part of maize grain.

granule according to Nägeli, but they have not been observed by Wiesner (Fig. 76).

In order to analyse the kinds of starch occurring in commerce, the Tables compiled for this purpose on the form and relative magnitude of the different kinds of starch by A. Tschirch,¹ and by A. Vogl,² may be specially recommended.

The size of the granules is determined, either by means of the micrometer, or by the very reliable weighing method devised by Schön. The procedure is as follows:—A small quantity of dried starch flour is placed under the microscope and the magnification so arranged that 20 small granules appear in the field. Their outlines are sketched

¹ *Real-Enzyklopädie der gesamten Pharmazie*, p. 137.

² See L. v. Wagner's *Stärkefabrikation*.

by means of a drawing apparatus, and the slide is then displaced in order to sketch a fresh number of the granules; this is repeated until 100 pictures are obtained, which are then carefully cut out with scissors, weighed, and the weight divided by 100. The average weight of a starch picture is thus obtained. In addition, a circular piece of the same paper of known diameter is weighed, and then from the diameter of the starch outlined paper, and taking into account the magnification, the diameter of the starch granule is determined.

Märcker has published the following compilation of the magnitudes of starch granules, from Wiesner's results:—

	Small granules.		Large granules.	
	Limiting value.	Usual value.	Limiting value.	Usual value.
	mm.	mm.	mm.	mm.
Barley . . .	0.0016—0.0064	0.0046	0.0108—0.0328	0.0203
Wheat . . .	0.0022—0.0082	0.0022	0.0111—0.0410	0.0282
Rye . . .	0.0022—0.0090	0.0063	0.0144—0.0475	0.0369

	Single granules.		Compound granules.	
	Limiting value.	Usual value.	Limiting value.	Usual value.
	mm.	mm.	mm.	mm.
Potato . . .	0.060 —0.100	0.070	—	—
Oats . . .	0.003 —0.011	0.003	0.014 —0.054	0.031
Rice . . .	0.003 —0.007	0.005	0.018 —0.036	0.022
Maize . . .	0.0072—0.0325	0.020	—	0.047

The following results were obtained in the laboratory of the Association of Spirit Manufacturers in Germany:—

	mm.
Average diameter of Kütriner starch, B.K.M.F. . . .	= 0.0355
Average diameter of Prima starch (Genthin) . . .	= 0.0328
Average diameter of Prima-waste starch (Genthin) . . .	= 0.0210
Average diameter of Secondary starch . . .	= 0.0169
Average diameter from the extraction of Secondary starch of the last washings.	= 0.0125
Average diameter from the corn swimming out on to the meadows from the outer reservoirs	= 0.0080

Estimation of the Content of Water in Starch.

The water-content of starch is very variable. It comprises that of potato starch mechanically freed from water; "green starch" still contains about 48-53 per cent. of water. Good commercial starch should not contain more than 20 per cent. of water; a direct determination of moisture is accordingly necessary.

The most accurate method of estimation is to weigh out 10 g. of

starch into a glass vessel provided with a stopper. It is heated first of all for an hour at 40° - 50° (gelatinisation would be produced if immediately heated to over 60°), and then dried for four hours at exactly 120° , allowed to cool in a desiccator, and again weighed. The loss in weight multiplied by 10 gives the percentage of water in the starch. According to Bondonneau, errors of from 2-3 per cent. occur by this method owing to the presence of acids which have found their way into the starch by fermentation, or have been added during the manufacture of the starch, since, on drying, sugar is formed, which retains $\frac{1}{10}$ of its weight of water. On the other hand, Saare¹ has proved that even with a content of 0.1 per cent. of sulphuric acid, which commercial starch could not possibly contain, the determination of water is not prejudiced. Even if sugar is formed, it is produced in so small a quantity that the water retained by it may be neglected. As, however, the formation of sugar is in no ways hindered by the addition of ammonia (advised by Bondonneau), this addition is superfluous, especially as it retards the drying by many hours.

As this method, which is doubtless the best and most accurate, takes too much time for practical use, other methods have been devised which permit of very rapid determinations of the water with sufficient accuracy for technical purposes.

Scheibler's method² depends on the observation that when 1 part of starch containing 11.4 per cent. of water is mixed with 2 parts of alcohol of 90 per cent. by volume (sp. gr. 0.8339), both substances remain unchanged, while starch containing more water gives up water to the alcohol, and starch containing less absorbs water from the alcohol.

In order to carry out the estimation, 41.7 g. of starch are weighed out into a glass-stoppered weighing-bottle, and 100 c.c. of alcohol of 90° Tralles added. The mixture is allowed to stand for one hour, with frequent shaking, filtered through a dry filter, and the specific gravity of the filtrate determined. The water-content of the starch is then read off from Table 55 (p. 676), calculated by Scheibler.

Scheibler has also constructed a hydrometer by which the water-content may be read off directly.

Saare's³ method of estimating the water depends on the fact that the specific gravity of absolutely dried starch is always equal to 1.65, i.e., 1 c.c. of starch = 1.65 g.

Since 1.65 g. of starch occupy a space of 1 c.c., then 100 g. of starch occupy a space of $\frac{100}{1.65} = 60.60$ c.c. If 100 g. of dry starch are placed in a 250 c.c. graduated flask, $250 - 60.60$ c.c., or 189.40 c.c. or g. of water

¹ *Z. Spiritusind.*, 1884, p. 595.

² *Dingl. polyt. J.*, 1868, 192, 504.

³ *Fabrikation der Kartoffelstärke*, p. 509.

will be required to fill it up to the mark, and the contents of the flask will weigh 289.40 g. Supposing that the starch is not dry, but contains 20 per cent. of water, then the 100 g. of starch taken for analysis should occupy a space of $48.5 + 20 \text{ c.c.} = 68.5 \text{ c.c.}$, since in the 100 g. there are 80 g. of dry starch occupying a space of $\frac{80}{1.65} = 48.5 \text{ c.c.}$ In order to make up to the mark, $250 - 68.5 = 181.5 \text{ c.c.}$ or g. of water would be needed, and the contents of the flask would now weigh $100 \text{ g.} + 181.5 \text{ g.}$

Table 55.

Table for Estimating the Content of Water in Starch. (Scheibler.)

Water-content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.	Water-content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.	Water-content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.
Per cent.			Per cent.			Per cent.		
0	93.3	0.8226	22	86.4	0.8455	44	79.7	0.8643
1	93.1	0.8234	23	86.1	0.8465	45	79.5	0.8651
2	92.9	0.8243	24	85.8	0.8474	46	79.2	0.8658
3	92.6	0.8253	25	85.5	0.8484	47	78.9	0.8665
4	92.3	0.8262	26	85.2	0.8493	48	78.6	0.8673
5	92.0	0.8271	27	84.9	0.8502	49	78.4	0.8680
6	91.7	0.8281	28	84.6	0.8511	50	78.1	0.8688
7	91.4	0.8291	29	84.3	0.8520	51	77.8	0.8695
8	91.2	0.8300	30	84.0	0.8529	52	77.5	0.8703
9	90.9	0.8311	31	83.7	0.8538	53	77.3	0.8710
10	90.5	0.8323	32	83.4	0.8547	54	77.1	0.8716
11	90.1	0.8335	33	83.1	0.8555	55	76.8	0.8723
12	89.8	0.8346	34	82.8	0.8563	56	76.5	0.8731
13	89.5	0.8358	35	82.5	0.8571	57	76.3	0.8738
14	89.1	0.8370	36	82.2	0.8579	58	76.0	0.8745
15	88.7	0.8382	37	81.9	0.8587	59	75.7	0.8753
16	88.3	0.8394	38	81.6	0.8595	60	75.4	0.8760
17	88.0	0.8405	39	81.3	0.8603	61	75.2	0.8767
18	87.7	0.8416	40	80.9	0.8612	62	74.9	0.8775
19	87.4	0.8426	41	80.6	0.8620	63	74.6	0.8783
20	87.1	0.8436	42	80.3	0.8627	64	74.3	0.8791
21	86.7	0.8446	43	80.0	0.8635	65	74.0	0.8798

= 281.5 g., from which it follows that the weight of the flask will be less the larger the percentage of water contained in the starch.

The estimation is carried out in the following manner:—100 g. of starch are weighed into a porcelain dish, stirred to a cream with distilled water, and washed into a 250 c.c. graduated flask of known weight; the flask is then made up to the mark at $17^{\circ}.5$ and weighed. The weight of the flask is deducted from this weight, and the starch-content corresponding to the weight thus obtained read off from Table 56 (p. 677).

The estimation carried out in this manner gives accurate results to within $\frac{1}{2}$ per cent. Still more accurate results are obtained if the flask, after being nearly adjusted, is allowed to stand for half an hour

in a larger vessel filled with water at 17°, and is then filled up to the mark. The method is only applicable to the determination of potato starch.

Finally, mention may be made of the method published by Bloch,¹ which is carried out by means of the apparatus constructed by him, called the "Fekulometer," which likewise, as its name suggests (fécule = potato starch), is only designed for the estimation of starch in potatoes. It is based on the assumption that 10 g. of absolutely dry starch, mixed

Table 56.

Table for Estimating the content of Water in Starch from its Specific Gravity. (Saare.)

Weight obtained.	Water-content of the starch.	Weight obtained.	Water-content of the starch.	Weight obtained.	Water-content of the starch.	Weight obtained.	Water-content of the starch.
g.	Per cent.	g.	Per cent.	g.	Per cent.	g.	Per cent.
289·40	0	283·10	16	277·20	31	271·25	46
289·00	1	282·70	17	276·80	32	270·90	47
288·60	2	282·30	18	276·40	33	270·50	48
288·20	3	281·90	19	276·00	34	270·10	49
287·80	4	281·50	20	275·60	35	269·70	50
287·40	5	281·10	21	275·20	36	269·30	51
287·05	6	280·75	22	274·80	37	268·90	52
286·65	7	280·35	23	274·40	38	268·50	53
286·25	8	279·95	24	274·05	39	268·10	54
285·85	9	279·55	25	273·65	40	267·75	55
285·45	10	279·15	26	273·25	41	267·35	56
285·05	11	278·75	27	272·85	42	266·95	57
284·65	12	278·35	28	272·45	43	266·55	58
284·25	13	277·95	29	272·05	44	266·15	59
283·90	14	277·60	30	271·65	45	265·75	60
283·50	15						

with water, always occupy the same volume of 17·567 c.c. after settling. If the starch contains water, then 10 g. will not absorb so much water, and therefore will occupy a correspondingly smaller space after settling. The Fekulometer gives, according to Bondonneau, accurate results with starches of good quality, but, on the contrary, very bad unreliable results with starches which have commenced to ferment or which contain impurities. According to Saare, the apparatus is constructed on the false principle that the volume which perfectly dry starch occupies on mixing with water is always the same, while on the contrary the volume depends on the size of the granules. Moreover, even small impurities must cause a different subsidence of the starch. The instrument gives, as a rule, with prima starch, 3-4 per cent. too much water; with starches containing much foreign matter, and gelatinised starch granules, the

¹ *Dingl. polyt. J.*, 1874, 211, 397.

results are much too low. The method is therefore unsuitable for analysis and is not to be recommended.

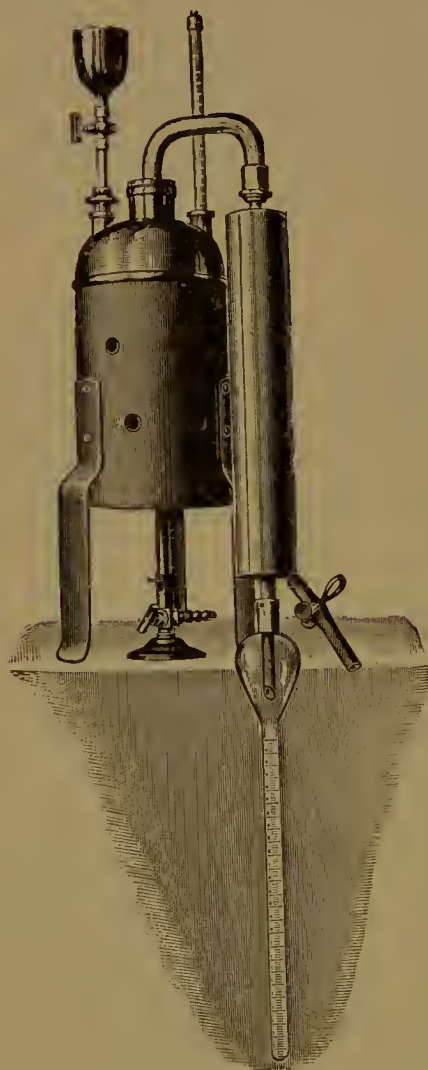


FIG. 77.

The estimation of water may be carried out rapidly and accurately in a very suitable manner with the apparatus constructed by J. F. Hoffmann and patented by the Institut für Gärungsgewerbe,¹ Berlin.

The apparatus (Fig. 77) consists of a distillation flask in which the substance for analysis is heated with oil whereby the contained water is driven off. The vapours pass through the distillation tube and are again condensed by thorough cooling. The oil and water then collect in a measuring tube placed under the condenser, from which the water-content may be directly read off.

According to Hoffmann's directions the estimation of water in starch flour is carried out as follows:—50 g. of starch are warmed with 400 c.c. of turpentine oil, to which 10 c.c. of toluene have been added, in the distillation flask for five minutes at 50°. The mixture is then heated up to 140° in five minutes, and maintained at this temperature so as to be able to raise it subsequently to 155° in four to five minutes. The burner is then removed, the apparatus allowed to cool to 140°, and the reading taken. The measuring tube is removed for this purpose, rolled to and fro several times

between the hands to remove the drops of water which cling to the glass, and a reading is taken at the point where the turpentine oil separates from the water underneath; an addition of 0.2 c.c. is made to the reading as a correction for the droplets of water suspended in the oil. The number obtained multiplied by 2 gives the percentage of water in the starch.

The estimation of water by this method gave results which agree very closely with those obtained by drying in an oven.

Estimation of Acid in Starch.

The starch is tested for acid by bringing on to the smoothly spread starch sample 1-3 drops of a neutral solution of purified litmus diluted

¹ Ger. Pat. 130295.

to a Bordeaux wine colour. If the starch becomes faintly blue or dark violet, it is free from acid; if wine-red, acid; and if brick-red, very acid.

In order to estimate the acid according to Saare, 25 g. of starch are pounded to a thick mash with 25-30 c.c. of water, and titrated with *N*/10 sodium hydroxide solution (1 c.c. = 0.004 g. SO_3) while vigorously stirring. The end-point is reached when 1 drop of the starch emulsion, placed on several folds of filter paper, is no longer coloured red with litmus. A similar thick emulsion of neutral starch serves as a control. If, for instance, 25 g. of starch require 1.8 c.c. of *N*/10 sodium hydroxide, then 100 g. will require 7.2 c.c. Accordingly as the starch requires 5, 8, or over 8 c.c. of *N*/10 sodium hydroxide, it is termed "slightly acid," "acid," or "strongly acid."

Determination of the Adhesiveness of Starch.

The higher the relative jelly tenacity, the greater the adhesiveness of starch. In order to estimate this tenacity Brown and Heron¹ determine the weight required to sink a thin glass plate into a paste prepared from 3 g. of starch and 100 c.c. of water. Dafert² estimates the time required for a certain quantity of paste of definite concentration to flow from a capillary tube. Thomson³ forms an opinion of the tenacity from the depth to which a falling body penetrates into the paste, falling from a height of 30 cm.

A more practical method is that due to Schreib.⁴ The starch is ground into an emulsion with water, and boiled thoroughly, with constant stirring, over an ordinary burner. As soon as the paste becomes transparent and immediately thereafter begins to froth up, it is removed from the flame, and well stirred for some time. The boiling must not last more than a minute. In this way Schreib obtained very satisfactory comparable results. By using 4 g. of starch and 50 c.c. of water, a normal starch should give, according to the cooling, a paste which will not pour out of the basin.

Examination of Starch Flour for Impurities and Adulterations.

The chief impurities of starch consist of sand and so-called specks which arise from coal-dust, soot, dust, residues from potato-skins, fungus mycella, dead algæ, particles of wood, threads from sacking, etc. The adulterations comprise the addition of a cheaper kind of starch to one of better quality, and probably, though rarely, the admixture of gypsum, chalk, and heavy spar.

¹ *J. Chem. Soc.*, 1879, 35, 596.

² *Landw. Jahrb.*, 1896, p. 259.

³ *Dingl. polyt. J.*, 1886, 261, 88.

⁴ *Kalender f. landw. Gewerbe*, 1899; *Z. angew. Chem.*, 1888, 1, 694.

To test for impurities, a weighed quantity of starch is either ignited, or it is dissolved and the residue examined. For the detection of insoluble mineral matter (sand), the solution may be obtained, either by warming with concentrated nitric acid, or by using an extract of malt after gelatinising the starch.

To recognise the kind of foreign matter present, the residue remaining after saccharification is examined under the microscope with a magnification of about 300 times.

To determine the number of specks, the method proposed by Saare may be used:—A sample of the starch is spread out smoothly on paper; a small glass plate of known area (*e.g.*, a microscope slide) is then laid on it, and the specks lying underneath counted. The sample is thoroughly mixed, the counting repeated several times, and the average taken. The number of specks is then calculated to 1 sq. dm.

Adulterations due to finely powdered mineral matter are easily recognised in the residue from the dissolved starch. A microscopical examination is the best way to detect adulterations produced by mixing with an inferior quality of starch.

C.—THE EXAMINATION OF THE WASTE PRODUCTS.

The waste products consist of residues which are used as cattle food, and the waste-water which is used partly for fertilising purposes, though often run off unused. A description of the methods for the examination of these products for their food and manurial values is outside the scope of this section. Since, however, starch unremoved by washing goes over with the pulp owing to defective working of the sieve and washing contrivances, and frequently considerable quantities of starch remain stored up in the unground or incompletely broken-up cells as bound starch, owing to indifferent grinding by friction or mill-stones, or incomplete opening up in other ways, a frequent examination of the pulp for starch as a control of the output from the starch manufactory is absolutely necessary.

In order to determine the starch unremoved by washing, 1 kg. of the pulp is washed with a large quantity of water through a horse-hair sieve, the effluent water poured through the finest silk gauze, and the starch deposited from this collected on a filter, dried first at 50° then at 120°, and weighed. To determine the unexposed starch, the thoroughly washed pulp residue is dried, and the absolute dry matter determined in one portion of the air-dried substance, by drying for about four hours at 100°-105°. The starch still present in this residue is then determined by one of the methods described above.

The total dry matter is made up of the dry matter found in thoroughly washed pulp, and the quantity of extracted starch found;

the total starch is obtained by addition of the bound starch obtained by analysis, and the starch removed by washing. The calculation is carried out as in the following example taken from Saare's *Die Fabrikation der Kartoffelstärke*.

From 1000 g. of pulp, 1.9540 g. = 0.195 per cent. of washed-out starch were obtained. The washed pulp weighed, air-dry, 198.9 g. = 19.89 per cent.; 100 g. of fresh pulp contained 19.89 g. air-dried matter, and a 100 g. of air-dried matter contained 84.36 g. of absolutely dry matter. The fresh pulp therefore contained $\frac{19.89 \times 84.36}{100} = 16.78$ per cent. of thoroughly washed water-free pulp, and $16.78 + 0.195 = 16.975$ per cent. of absolutely dry matter. Further, 52.5 per cent. of starch was found in 3 g. of the air-dried washed pulp. The water-free matter therefore contained $\frac{52.5 \times 100}{84.36} = 62.23$ per cent. of bound starch, and the fresh pulp $\frac{62.23 \times 16.78}{100} = 10.44$ per cent.

The following is therefore the composition of the pulp:—

	Per cent.
Water	83.02
Dry matter	16.98
Starch, unremoved by washing	0.19
Bound starch	10.44
Total starch	10.63

Accordingly the thoroughly washed water-free pulp contained 62.23 per cent. of starch and the total starch, obtained by washing 1.83 per cent. of starch unremoved by washing.

The percentage of bound starch in the dried pulp substance should not, as a rule, exceed 60 per cent.; the content of starch unremoved by washing in the total starch should be, at most, 5 per cent.

D.—THE EXAMINATION OF THE AUXILIARY RAW MATERIALS USED IN THE MANUFACTURE OF STARCH.

The water used in the manufacture is the main point to be considered. It must be colourless, odourless, and without suspended solids, and as free as possible from ferrous salts. Moreover, it should show no signs of putrefaction and should not be too hard. The water must be analysed in respect of all these properties before it can be used in the manufacture of starch. The details concerning the methods of analysis are given in the section on "Drinking Water and Water Supplies," Vol. I., Part II., pp. 732 *et seq.* The tests of purity of the chemicals used in the manufacture of starch, such as caustic alkalis, sodium carbonate, hydrochloric acid, and sulphurous acid are fully described in the respective sections dealing with these products.

II. DEXTRIN.

The analyses relating to dextrin and its manufacture comprise:
1. The raw materials used for the manufacture. 2. The auxiliary raw materials.* 3. The control of the working conditions. 4. The manufactured product.

A.—THE EXAMINATION OF THE RAW MATERIALS.

The raw materials, of which the most important are potato starch, and wheat and maize starches, are examined for their origin, quality, and purity by the methods described in connection with Starch.

B.—THE EXAMINATION OF AUXILIARY RAW MATERIALS.

Dilute acids (nitric acid, hydrochloric acid, sulphuric acid, oxalic acid, lactic acid, etc.) are used as auxiliary raw materials. These are tested for their purity, especially sulphuric acid, nitric acid, and hydrochloric acid for a possible content of arsenic, and hydrochloric acid and nitric acid for the possible presence of free chlorine. The tests are carried out in the usual way, as described under the respective sections in Vol. I.

C.—THE CONTROL OF WORKING CONDITIONS.

A constant control of the accurate progress of the process of dextrin formation is of great importance for regulating the working of the factory. It is effected either by determining the degree of solubility in water of the roasted products, or by the iodine reaction.

For estimating the solubility in water, Lippmann¹ recommends the following process:—20 g. of the sample for analysis is mixed in a 500 c.c. flask with 200 c.c. of water; in order to avoid agglomeration, it is best to put 100 c.c. of water into the flask and then, while shaking, to add the dextrin and finally the remaining 100 c.c. of water. The flask is efficiently stoppered, thoroughly shaken for five minutes, the contents filtered through a dry filter, and the specific gravity of the filtrate determined with Balling's hydrometer. The degrees registered by the hydrometer multiplied by 10 gives the percentage soluble in cold water. This method is accurate to within 2-3 per cent., which is quite sufficient for control purposes, since it is only in rare cases that differences of a few per cent. are of importance in the case of dextrans where the cold water solubility varies between 20 and 90 per cent.

The iodine reaction is carried out, according to the method described by Saare,² as follows:—0.1 g. of the sample for analysis is weighed out

¹ *Z. Spiritusind.*, 1902, Nos. 22-29.

² *Ibid.*, 1900, No. 7.

on a small hand balance, shaken into a large test tube graduated at 100 c.c., mixed with about 5 c.c. of water, dissolved by boiling, and diluted to 100 c.c. with cold water. It is then mixed with 1 drop of $N/10$ iodine solution, either in the test tube, or after pouring into a suitable glass cylinder if a series of samples are to be compared. The coloration of the falling drop is observed, the solution shaken, and the coloration again noted. The following valuations were found in tests which were removed from a Gommeline roasting at equal intervals of time:—

Falling drop.			After shaking.			Solubility in water of 100 parts of water-free dextrin. Per cent.
No. 1.	Blue	.	Blue	.	.	0
No. 2.	Brighter blue	.	.	0.1
No. 3.	Violet-blue	15.2
No. 4.	Violet	.	Violet	.	.	39.2
No. 5.	Violet-red	.	Strongly violet	.	.	49.5
No. 6.	Reddish-brown	.	Colourless	.	.	62.5

If several drops of iodine solution are added, the colours are slightly changed and No. 6 becomes wine-red. It is obvious that certain shades of colour will be distinctive for the different varieties of dextrans, and may be easily established for every individual case, according to the method of working.

D.—ANALYSIS OF DEXTRIN.

The analysis of commercial dextrin comprises principally the following estimations:—The percentage of pure dextrin, of water, the acidity; the percentage of ash and sand, of constituents soluble and insoluble in cold and hot water, of soluble starch and sugar; the consistency and the permanence of the concentrated solution; the viscosity and the percentage of chlorine, of unaltered starch, and of gluten.

1. *Estimation of the Percentage of Pure Dextrin.*—This may be made indirectly by estimating the amount of sugar and ash in the cold water solution and deducting this from the quantity of dextrin taken for analysis.

For the direct estimation of the pure dextrin in commercial dextrans, Roussins' method is used, which is based on the insolubility of pure dextrin in strong and its solubility in dilute alcohol. To carry out the estimation the aqueous solution of a weighed amount of dextrin, evaporated to a syrupy consistency, is mixed with ten times its volume of 90 per cent. alcohol, and the precipitated dextrin washed with similar alcohol, dried, and weighed. 1 g. of the dextrin is dissolved in 10 c.c. of water and the solution mixed with 30 c.c. of 56 per cent. alcohol, 4 drops of 26 per cent. ferric chloride solution, and a few decigrams of powdered chalk (for the precipitation of any gum present which

combines with ferric hydroxide). The residue is filtered after thorough stirring, washed on the filter paper with 56 per cent. alcohol, and the dextrin precipitated from the filtrate with 96 per cent. alcohol. After twenty-four hours, the alcohol is decanted, the dextrin dissolved in a small quantity of water, and the solution evaporated to dryness in a weighed dish; from the quantity of pure dextrin thus obtained the percentage of pure dextrin in the sample may be readily calculated.

2. *For the Estimation of the Water*, about 2-3 g. are placed in a U drying tube, and heated to constant weight in an oil-bath at 110° in a current of air, completely dried by passing through sulphuric acid. The content of water is calculated from the loss in weight. The method is not free from objection. On the one hand, the temperature of 110° is so high that a fairly considerable amount of coloration and decomposition of the dextrin is unavoidable. On the other hand, it is impossible to dry the dextrin to constant weight as directed, on account of the changes which the dextrin undergoes in drying, which are really a continuation of the roasting process. In addition, drying of the dextrin in a current of dry air is somewhat tedious.

Saare's method¹ is very much simpler and altogether reliable. 10 g. of dextrin are dried for four hours at 105° ; the difference in weight multiplied by 10 gives the percentage of water.

According to a later proposal by Hefelmann and Schmitz-Dumont,² 2 g. of dextrin, dissolved in a little water, are weighed into a small porcelain dish containing a glass rod and ignited sand, evaporated to dryness on the water-bath, and the residue dried for four hours at 105° .

3. *The Acidity of Dextrin* is determined by titrating, in the cold, with $N/1$ sodium hydroxide, 100 g. of dextrin dissolved in five to ten times the quantity of water. The number of cubic centimetres of $N/1$ sodium hydroxide required gives the degree of acidity; this should not exceed 5 c.c.

4. *The Percentage of Ash* is obtained by igniting 10 g. of dextrin in a platinum crucible; the last traces of carbon can be removed, if necessary, by moistening with ammonium nitrate and igniting. Prima dextrin should not give more than 0.5 per cent. of ash.

5. *The Content of Sand* can be estimated either by dissolving the ash in hydrochloric acid, or 100 g. of dextrin are boiled in a beaker with water and after complete solution the liquid is allowed to stand, when the sand is deposited. The solution of dextrin is then cautiously decanted, the sand washed several times with distilled water, washed into a platinum basin, evaporated to dryness, and ignited. The sand in prima dextrin should not amount to more than 0.2 per cent.

6. *Estimation of the Constituents of Dextrin Soluble and Insoluble in*

¹ *Kalender f. d. landw. Gewerbe*, published by the Verein d. Spiritusfabrikation, 1910.

² *Zeits. öffentl. Chem.*, 1898, 13.

Cold and Hot Water.—The matter soluble in cold water is estimated as follows according to Saare¹:—300 c.c. of water at 17°·5 are poured on to 30 g. of dextrin, allowed to stand, with occasional shaking until the lumps have disappeared, and filtered; 5 c.c. of the filtrate are weighed off, evaporated to constant weight, and again weighed. The content of dry substance in 100 g. of the liquid is calculated from the result.

The following very exact method is due to Hefelmann and Schmitz-Dumont²:—5 g. of dextrin are dissolved in cold water in a 250 c.c. flask, which is then made up to the mark; 100 c.c. of this solution are transferred to a 110 c.c. flask, 7 c.c. of ether added, and the flask corked and well shaken. The starch agglomerates into a flocculent precipitate, while the whole of the dextrin remains in solution. After standing for a short time, this is filtered through a covered pleated filter, 50 c.c. of the filtrate (corresponding to 0·945 g. of dextrin) evaporated to dryness on the water-bath in a dish containing sand, and the residue dried for four hours at 105°. The increase in weight of the sand and dish gives the soluble matter.

When it is only a question of determining the solubility approximately, Lippmann's method (see p. 682) may be used.

The quantity of matter insoluble in cold water is obtained from the difference between the original substance and that soluble in cold water. For its direct estimation 30 g. of dextrin dissolved by shaking in ten times its weight of water is filtered through a filter, which has been dried and weighed at 100°, and washed with distilled water until a drop of the filtrate no longer gives a residue on evaporating it to dryness on platinum foil. By weighing the dried filter and deducting the weight of the filter paper, the weight of the matter insoluble in cold water is obtained. This consists principally of soluble starch (besides organic impurities and sand).

To estimate the matter soluble and insoluble in hot water, the dextrin is boiled with water instead of being shaken with cold water. If the residue show appreciable quantities of starch paste, it points to unconverted starch in the dextrin. The filtered residue is then converted into sugar and the sugar determined according to the recognised methods and calculated as starch.

7. *The Soluble Starch* contained in the portion insoluble in cold water is also determined in the same way as unconverted starch, by converting it into sugar, determining the sugar, and recalculating into starch.

8. *The Sugar* always present in commercial dextrin, which is contained in the portion of the dextrin analysis soluble in cold water, may be either maltose or dextrose. These sugars, according to Post,

¹ *Kalender f. d. landw. Gewerbe*, 1910, p. 138.

² *Zeits. öffentl. Chem.*, 1898, 4, 448.

may be distinguished by means of Barfoed's Reagent (13.3 g. neutral copper acetate dissolved in 5 c.c. of 35 per cent. acetic acid and 200 c.c. of water). This solution is immediately reduced on warming by the smallest trace of dextrin, or after a short time in the cold, with the separation of cuprous oxide, while maltose (according to Märcker's observations) produces a slow and slight reduction of the copper solution, and this only in concentrated solution and on standing. Maltose is estimated by Fehling's solution, care being taken that the solution does not contain more than 1 per cent. of maltose, that an excess of undiluted Fehling's solution is present, and further, that the liquids (according to Soxhlet) are maintained vigorously boiling for four minutes. Any dextrose present is determined and calculated as maltose.

According to Hefelmann and Schmitz-Dumont,¹ 25 c.c. of the ether-water solution obtained in their method of determining the portion soluble in cold water (p. 685) are treated with Fehling's solution, and the separated cuprous oxide is collected in a Gooch crucible, as recommended by Hefelmann, converted into cupric oxide by single ignition over a Teclu burner, and calculated to maltose.

9. *For the Determination of the Keeping Quality and Consistency of the Concentrated Solution*, which serve for comparison and possible identification of two dextrin samples, Lippmann² has proposed the following procedure:—30 g. of each of the samples to be compared are boiled with 30 c.c. of water in a porcelain dish over a free flame (gas or spirit flame), with constant stirring, until the solutions are completely homogeneous. The solutions after cooling are compared as regards consistency, adhesiveness, or ropery effect on a small piece of wood, and also as regards their other properties. The keeping quality is determined by allowing them to stand for several days in air as free as possible from germs. Many dextrans which dry quickly crack on the surface and lose their elasticity and adhesiveness (property of pulling out into threads) even after a short time, while others remain unchanged for several days.

10. *The Determination of the Viscosity* is useful for identifying two dextrans. This may be carried out, according to Lippmann,³ as follows:—10 g. of dextrin are stirred or shaken with five times their weight of water, until the water-soluble portion is dissolved, and then filtered through a dry filter. An aliquot part of the filtrate is then tested in the viscometer for its rate of flow. The Engler viscometer for lubricating oil can be used for this determination (see section on "Lubricating Oils," this Vol., p. 68).

11. *Chlorine*.—Dextrans containing free chlorine or hypochlorous

¹ *Zeits. öffentl. Chem.*, 1898, 4, 448.

² *Z. Spiritusind.*, 1902, No. 29.

³ *Ibid.*, 1902, p. 304.

acid are unsuitable for many technical purposes. An examination for chlorine is on this account necessary.

12. *Unchanged Starch*.—Commercial dextrin must be free from unchanged starch. This can be detected either by boiling the sample, when the formation of starch paste will show the presence of unchanged starch, or by treating the sample with a fairly dilute solution of potassium or sodium hydroxide, when the dextrin and soluble starch will dissolve to a clear solution, while unchanged starch, on the contrary, will produce a viscous paste.

13. *Scorched Glutin*.—Dextrins prepared from wheat starch, particularly from the residues of the manufacture of wheat starch, not infrequently contain a considerable quantity of gluten, which scorches and becomes hard in the roasting process, so that the dextrin is unsuitable for many purposes. In order to determine the scorched gluten, Brenner¹ stirs 1 part of dextrin with 1 part of water at 60°, and then adds a further 5 parts of water at the same temperature. The mixture is allowed to stand for twenty-four hours. The scorched gluten swells up and deposits on the bottom without itself dissolving in the liquid or causing the latter to thicken.

Addendum.—W. A. Davies and A. J. Daish² have shown that the O'Sullivan method (p. 660) gives approximately accurate results with purified starch, but that with plant material in general the results are 15-20 per cent. too low, owing to the precipitation of dextrin when basic lead acetate is used as a defecating agent. They have elaborated a method in which the starch is hydrolysed to a mixture of dextrose and maltose by Taka diastase. The dry material (free from sugars and if necessary previously saturated with water) is gelatinised with 200 c.c. of water, the liquid cooled to 38°, and 0.1 g. of Taka diastase together with 2 c.c. of toluene added. This mixture is incubated at 38° for twenty-four hours and the clear liquid above the plant material is filtered into a 500 c.c. flask. The residue is washed repeatedly by decantation and the washings poured through the filter paper. The volume is then made up to 500 c.c., and the percentage of dextrose and maltose estimated by the copper reduction and polarimetric methods. The percentage of these two sugars found is then calculated to starch.

¹ Muspratt, *Die Chemie und ihre Anwendung*, 3rd ed., vol. iii., p. 332.

² *J. Agric. Sci.*, 1914, 6, 152.

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ALCOHOL, POTABLE SPIRITS, AND LIQUEURS¹

By A. EBERTZ, Ph.D., and G. SCHÜLE, Ph.D. English translation revised by
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I. THE EXAMINATION OF WATER.

AN analysis, both chemical and bacteriological, of the water used in distilleries may be necessary when there is reason to suspect the presence either of substances which may inhibit fermentation, or of organisms which may give rise to undesirable decompositions during the process of fermentation. Water destined to be used for the dilution of potable spirits should be as pure as possible. The turbidity which is often produced on dilution of distilled spirits may be due either to the use of too hard a water, or to the presence of a high proportion of fusel oil in the spirit. Methods for the examination of water are fully described in the section on "Drinking Water and Water Supplies," Vol. I., Part II., pp. 732 *et seq.*

II. THE EXAMINATION OF RAW MATERIALS.

A.—AMYLACEOUS MATERIALS.

The various methods of estimating starch in cereal grains are all based, in the first place, upon the hydrolysis or conversion of the starch molecule, either by means of acids or by the diastase of malt.

When acids are used to effect the conversion, their action may be arrested at a point corresponding to the production of soluble starch, which may then be estimated by means of the polarimeter, or the conversion may be carried further until the whole of the starch has been transformed into dextrose. The dextrose is then estimated by means of Fehling's solution.

When the conversion is effected by the diastase of malt, a mixture

¹ In the German edition the subject matter of this section is divided into the two separate sections of "Alcohol" by Dr A. Ebertz, and of "Brandy and Liqueurs" by Dr G. Schüle. In view of the conditions of work obtaining in this country, it has been considered preferable to combine these two sections under the heading of "Alcohol, Potable Spirits, and Liqueurs."—C. A. K.

of starch degradation products is obtained. If the conversion is carried out under strictly defined conditions, the resulting products are maltose and a stable dextrin, the relative proportions of which may be estimated from the copper reduction together with the rotation. If the solution resulting from the action of diastase is boiled with hydrochloric acid, the whole of the starch originally present is converted into dextrose, as in the direct acid hydrolysis method.

Lastly, the solution containing maltose and dextrin may be completely fermented with yeast in the presence of active diastase, and the original percentage of starch calculated from the amount of alcohol produced.

The estimation of starch by direct acid conversion, with complete hydrolysis to dextrose, is only possible when no "cellulose" is present. In the case of cereal grains containing cellulose, boiling with hydrochloric acid is liable to dissolve a considerable quantity of pentosans and hemicelluloses, and to hydrolyse them to reducing sugars. The solution and hydrolysis of pentosans may also occur to some extent, as has been shown by Lintner, when the diastase method is employed. This objection does not apply in the same degree to those methods in which the starch is estimated polarimetrically after partial hydrolysis with acids, as, although pentosans, etc., may pass into solution, the error thus introduced is not so large as is the case when the estimation is carried out by Fehling's solution after complete hydrolysis to dextrose.

I. The Polarimetric Estimation of Starch in Cereals.

This method, originally proposed by Dubrunfaut, has been shown by Lintner to be both rapid and reliable. According to L. T. Thorne and E. H. Jeffers,¹ the best results are obtained by the following procedure:—5 g. of material, previously reduced to the finest possible state of division, are placed in a mortar and triturated with successive small additions of water till the mixture just ceases to cling to the pestle in lumps. This generally requires less than 20 c.c. of water. Hydrochloric acid of sp. gr. 1.15 is then added, with continued trituration, in portions of about 5 c.c. at a time, until the mass first swells up into a jelly, and finally breaks down into a somewhat viscous liquid. This requires about twice as much acid as the water first used, unless the original material contained much moisture, when the quantity of acid required is somewhat greater. The mixture is allowed to stand for about ten minutes, and is then transferred to a 200 c.c. calibrated flask, into which has previously been measured 10 c.c. of a 4 per cent. phosphotungstic acid solution and 20 c.c. of hydrochloric acid of

¹ 7th Internat. Congress of Applied Chemistry, 1909, section vi., A., p. 14.

sp. gr. 1.15. The mortar is rinsed with dilute hydrochloric acid (sp. gr. 1.1), and the whole made up to 200 c.c. with dilute (1.1) acid. After mixing, the contents of the flask are transferred to a wide-necked, stoppered bottle, and thoroughly shaken (or placed in a centrifugal machine) till a well-defined flocculent precipitate is obtained and the supernatant liquid is fairly bright. After filtration, the polarimetric reading of the solution is taken. With a 200 mm. tube, the Schmidt-Haensch scale and white light, the percentage of starch is given by the formula :—

$$P = \frac{R \times 40}{11.6}$$

where P is the percentage of starch present, and R = the polarimeter reading. If any other polarimeter scale is used, the amount of soluble starch present is calculated on the assumption that $[\alpha]_D = 200^\circ.3$ for barley starch, being approximately the same for all cereal starches.

Several other methods of estimating starch by the polarimeter have been published, various acids such as picric,¹ trichloroacetic,² sulphuric,³ and acetic acids⁴ being employed for the hydrolysis, but none of them appear to possess any advantages over the method given above. (*Cf.* the section on "Starch and Dextrin," this Vol., pp. 667 *et seq.*)

2. The Estimation of Starch by Hydrolysis with Diastase.

This method, as originated by C. O'Sullivan in 1884,⁵ consists essentially in extracting the finely divided grain in the first instance with ether for the separation of the fats, and afterwards with alcohol of sp. gr. 0.90 at a temperature of 35°-38° for the complete separation of the sugars. The residue from the alcohol treatment is then thoroughly washed with water at 35°-38° until the amylans are completely removed, and after this the starch-containing residue is boiled with water, cooled to 62°-63°, and digested for an hour with a little diastase until the whole of the starch is hydrolysed. The maltose and dextrin are then determined in the filtrate from a consideration of the polarimetric reading and the cupric reducing power, the specific gravity of the liquid, corrected for the diastase used, being employed as a quantitative check. From the amount of the hydrolysed starch products so determined, the amount of starch is calculated.

The method is a tedious one, as the complete removal of the soluble non-starchy matter by washing with alcohol and water is a process often requiring several days. H. T. Brown and J. H. Millar⁶ have modified the

¹ M. Buisson, 7th Internat. Congress of Applied Chemistry 1909, section vi., A, p. 15.

² P. Biourge, *Bull. de Bras.*, 1909, p. 22; *Chem. Zeit. Rep.*, 1909, 33, 446.

³ Wenglein, *Z. ges. Brauw.*, 1908, 31, 53.

⁴ E. Ewers, *Zeits. öffentl. Chem.*, 1908, 14, 8.

⁵ *J. Chem. Soc.*, 1884, 45, 1.

⁶ *Trans. Guinness Research Laboratory*, 1903, vol. i., part i., p. 79.

method so that a starch estimation in barley can be carried out in five hours, and in malt in ten to eleven hours. They dispense altogether with a polarimetric reading, and utilise the fact that when starch is acted upon by an active malt extract of 80° Lintner for sixty minutes, the products of conversion consist of 80.8 per cent. of maltose and 19.2 per cent. of a stable dextrin. Inasmuch as the amylans are not hydrolysed to cupric-reducing substances under these conditions, it is not necessary to remove them by washing.

To carry out the estimation, about 5 g. of the finely ground grain are weighed out into a paper thimble and extracted with alcohol of sp. gr. 0.900 in a Soxhlet extraction apparatus. In order that alcohol of the requisite strength shall distil into the upper part of the extractor, the alcohol in the flask is of a gravity of 0.920. For 5 g. of material 80 c.c. of alcohol are used. The temperature of the alcohol in the extractor should be maintained at approximately 40°, and the extraction carried out for three hours in the case of barley and nine hours for malt, owing to its higher content of reducing sugars.

The contents of the thimble are then transferred to a beaker containing about 100 c.c. of water, and the whole thoroughly boiled. After cooling to 57°, 10 c.c. of an active malt extract are added, and the conversion allowed to proceed for sixty minutes. The solution is then boiled, filtered into a 200 c.c. flask, the residue well washed, and the volume adjusted after cooling. The cupric reduction of 20 c.c. of the solution is determined, and the maltose calculated from the copper reduced after correction for the reduction due to the malt extract. The starch equivalent to this maltose is then ascertained, on the assumption that 84.4 parts of maltose correspond to 100 parts of starch. The malt used should have a diastatic power of 80° Lintner, and if the activity of the malt extract is not sufficient to convert the starch products down to the point at which 84.4 parts of maltose are formed from 100 parts of starch, due allowance must be made for this. If malt of a diastatic capacity of only 40° Lintner is used, the final step in the reaction is reached when 82.5 parts of maltose have been formed from 100 parts of starch instead of 84.4 parts. If malt of a higher diastatic capacity than 80° Lintner is used, the starch is apt to be over-converted, and irregular results are obtained.

A modification of the diastase method which is much used is the following:—About 5 g. of the fat-free, dry material are washed on a filter with 150 c.c. of 10 per cent. alcohol, and then with 10 c.c. of 95 per cent. alcohol. The residue is placed in a beaker with 50 c.c. of water, and the beaker immersed in boiling water and stirred constantly for fifteen minutes till all the starch is gelatinised. It is then cooled to 55°, 20-40 c.c. of malt extract added, and the temperature maintained at 55°, until no more starch can be detected in the residue when tested

with iodine. The liquid is then cooled, transferred to a 250 c.c. flask, and made up to the mark. 200 c.c. of the filtrate are mixed with 20 c.c. of hydrochloric acid (sp. gr. 1.125), and heated in a boiling water-bath under a reflux condenser for two and a half hours. The mixture is cooled, nearly neutralised with sodium hydroxide, and made up to 500 c.c. The dextrose is then determined in an aliquot part of the solution. The percentage of starch is found from that of dextrose by multiplying by 0.9.

The malt extract is prepared by digesting 10 g. of finely ground malt with 200 c.c. of water for two or three hours at the ordinary temperature, and filtering. The amount of dextrose yielded by a given quantity of the filtrate after boiling with hydrochloric acid under the same conditions as given above must be determined, and the necessary correction made in the starch estimation.

3. The Estimation of Starch by Fermentation.

In the fermentation method 5 g. of the fat-free sample are extracted with alcohol as above, the residue washed into a flask and thoroughly boiled to remove alcohol and to gelatinise the starch. The starch is then converted with 6 c.c. of an active malt extract and fermented for several days at 26°-27° with 2 g. of yeast without previous destruction of the diastase. A check solution with yeast, malt extract, and water is kept under similar conditions, and the alcohol produced allowed for. The alcohol is estimated from the specific gravity of the distillate after fermentation is complete.

92 parts of alcohol are equivalent to 153.9 parts of starch.

In distilleries where the conversion of maize or raw grain is carried out under pressure or by an acid conversion process, more satisfactory results will be obtained by carrying out the starch conversion in the laboratory as far as possible under analogous conditions, combined with a fermentation experiment on the lines indicated above, using not less than 50 g. of material. When carefully carried out, such experimental mashes are capable of giving valuable information as to the probable behaviour of the material, the ease with which it is fermented, and the yield of alcohol to be expected.

B.—MOLASSES.

1. The Estimation of Fermentable Sugars.

The usual methods of analysis of sugars (see section on "Sugar," pp. 578 *et seq.*), polarisation and copper reduction, when applied to the valuation of molasses for distilling purposes, do not give reliable results from the point of view of the distiller. It has been shown by G. Harker¹

¹ *J. Soc. Chem. Ind.*, 1906, 25, 831.

that the possible yield of alcohol from cane molasses indicated by analysis is considerably higher than that which can actually be obtained by fermentation, and that the analytical figures apparently overstate the amount of fermentable sugars actually present. The results obtained must therefore be submitted to a correction which depends upon the amount of non-fermentable reducing sugars remaining in the liquid after inversion, and which is considerably greater when the inversion is effected by acids than when invertase is used. The calculation of the probable yield of alcohol from the results of analysis of molasses would appear to depend to some extent upon certain factors not yet fully understood.

For the purposes of the distiller, the most suitable method of determining the content of fermentable sugar in a sample of molasses consists in estimating the alcohol actually obtained by fermentation. Although this procedure affords no information as to the nature and proportions of the different sugars present in the molasses, it supplies valuable information as to the yield of alcohol which may be expected, and the readiness with which the sample in question undergoes fermentation.

According to Delbrück, the fermentation experiment is most conveniently carried out in the following manner:—250 g. of the sample are diluted with water to 1 litre and the sugar-content of the solution approximately determined by means of the saccharometer. If the molasses is alkaline, it is acidified with $N/1$ sulphuric acid until the solution contains 1.5 c.c. of $N/1$ acid in every 100 c.c. Three portions of 100 c.c. are withdrawn and weighed. Two of them are boiled for half an hour and made up again with water to their original weight, and to one of these is added 0.5 g. of wheat bran. All three portions are then introduced into distilling flasks provided with fermentation seals and fermented with pure yeast (1 g. yeast to each flask) until no further loss in weight takes place. After the addition of 100 c.c. of water to each flask the contents are distilled until no more alcohol passes over. The alcohol is determined in the distillate in the usual manner (see p. 709), and the yield calculated on the original sample. 0.6783 litres of alcohol correspond to 1 kg. of cane sugar. The average yield of alcohol from molasses is $6\frac{1}{4}$ proof gallons per cwt., or approximately 560 c.c. of proof spirit per kg. of molasses.

2. The Fermentative Capacity.

Many samples of molasses undergo fermentation with difficulty, a condition which may be caused by the presence of volatile fatty acids, or, less frequently, of nitrous acid (Märcker and Neale).

In the free state these acids have a marked toxic action on yeast, and exercise, even in very small quantities, a prejudicial effect on the

growth and fermenting power of the yeast. According to Neale, the content of molasses in volatile acids should not exceed 0.5 per cent.

If the fermentation test has shown that the molasses in question ferments with difficulty, the volatile fatty acids should be determined in the following manner:—50 g. of the sample are diluted with 200 c.c. of water, 10 c.c. of concentrated sulphuric acid added, and the mixture distilled until 100 c.c. have passed over. (The distillation must not be carried further, or formic acid may be produced by the action of sulphuric acid on the lævulose present.)

The distillate is mixed with a slight excess of baryta water, and the excess of baryta precipitated by passing carbon dioxide through the warm liquid. The liquid is then boiled, and the precipitated barium carbonate filtered off. The filtrate is evaporated and the residue transferred to a platinum dish, dried at 130° , and weighed. The dry residue is then ignited until the organic matter is burnt off and the ash is quite white. After moistening with ammonium carbonate solution, evaporating again to dryness and gently igniting, it is again weighed. From the difference between the two weights the quantity of organic acids present in the original sample is calculated. In the distillate, butyric acid may be detected by its odour, formic acid by the production of a mirror of reduced silver when warmed with an alkaline silver solution, and nitrous acid by the colour produced on addition of a starch solution containing potassium iodide, or by an acetic acid solution of sulphanilic acid and α -naphthylamine hydrochloride.

More frequently the inhibition of fermentation is due to the presence of micro-organisms. In cases where this is suspected, it may be established by a fermentation experiment carried out as described above. Hinzelmann prefers to take portions of 500 c.c. of the diluted sample, and to acidify one portion before boiling to the extent of 3.0-3.5 c.c. of $N/1$ acid per 100 c.c. The more strongly the molasses is acidified, the more easily are the micro-organisms killed on boiling. To each portion of 500 c.c. are added 2 g. of pure yeast, and 2.5 g. of wheat bran, and the fermentation allowed to proceed at 25° . The progress of the fermentation is followed by weighing the flasks at intervals of twenty-four, forty-eight and seventy-two hours, and eventually measuring the degree of attenuation by means of a specific gravity determination. By such experiments indications may often be obtained as to the preliminary treatment necessary before the molasses is subjected to fermentation in the distillery.

In molasses which contain a considerable quantity of potassium nitrate, nitrous acid may be formed by the reducing action of certain micro-organisms, with the result that fermentation is suppressed or seriously inhibited. The determination of nitric acid or nitrates in molasses may be carried out by the usual methods (Vol. I., p. 311).

C.—OTHER RAW MATERIALS.

By far the greater part of the alcohol produced in Great Britain, whether destined for potable or industrial use, is made from malt and unmalted grain, and molasses. The quantity produced from potatoes and other materials is comparatively insignificant. A variety of raw materials has been used in the past at various times, but at present it may be said that the only ones of any importance other than malt, grain, and molasses, are sugar, rice, glucose, and sago.

The estimation of starch and sugar in these materials may be carried out substantially according to the methods described above (*cf.* also the sections on "Starch and Dextrin," and on "Sugar," this Vol., pp. 658 and 539. The estimation of sugars is described in the section on "Brewing Materials and Beer," this Vol., pp. 824 *et seq.*).

Wort Extract and Spirit Yield of Mashing Materials.

For the purposes of the distiller, information as to the amount of extract and alcohol obtainable from his material is usually of more value than a knowledge of its starch and sugar content. This information may be obtained by carrying out the operations of mashing and fermenting on a small scale, adhering as closely as possible to the actual working conditions of the distillery. The following example of such a miniature mash as carried out in the laboratory will indicate the method employed as applied to flaked maize:—40 g. of flaked maize were mixed with about 250 c.c. of water, the mixture raised to the boiling point and then cooled to 60°. 10 g. of malt grist were then well stirred in, and the mashing process allowed to proceed at a temperature of 57°-60° for one and a half hours. The mash was then raised gradually to 68°, and the whole of the wort drained off from the grains. The grains were then washed with small quantities of water to remove all the wort, the quantity of water used being sufficient to bring the total volume of the wort up to 300 c.c. The gravity was then determined at a temperature of 15° and found to be 1049. The degrees of gravity above 1000, multiplied by 11.2 and divided by the number of grams of material used for each 100 c.c. of wort collected, will give the quantity of extract in brewing pounds per cwt., which is the equivalent expression in the practical scale. In the above case, 50 g. of material produced 300 c.c. of wort at a gravity of 1049; the extract was therefore:—

$$(49 \times 11.2) \div \frac{50}{3} = 32.9 \text{ brewing pounds per cwt.}$$

The collected bulk wort was then fermented with yeast for sixty hours at a mean temperature of 28°. On distillation of the wash,

100 c.c. of distillate were obtained at a sp. gr. of 0.98015, equivalent to a liquid containing 27.7 per cent. of proof spirit. This on calculating out showed a yield of 6.27 proof gallons for 1 cwt. of the mixture of materials.

D.—THE EXAMINATION OF BARLEY AND MALT.

I. BARLEY.

An important factor in selecting a barley for the production of distillery malt, especially where patent stills are employed, is the amount of diastase that is produced on germination. The determination of the vegetative capacity is therefore one of the most important tests to be applied. A large proportion of dead corns not only cause a lower yield of diastase, but favour the growth of moulds and of micro-organisms which may exert a prejudicial influence on the course of fermentation.

The method of determining the vegetative capacity is described in the section on "Brewing Materials and Beer," this Vol., p. 821. A sample of barley may be considered as good when the vegetative capacity is 95 per cent. or over, moderate if 90-95 per cent., inferior if 80-90 per cent., and bad if less than 80 per cent.

A good sample of barley should possess a fresh and sweet smell, not musty or mouldy. It should be of a light straw-yellow colour and be free from mould. The tips should be of the same colour as the rest of the corn; corns with blackened tips are the result of overheating in the stack. Such barley will germinate badly and the germinating power will decrease still further on storage. It should be as free as possible from foreign seeds and broken or damaged corns, which are favourable to the growth of moulds. The grains should be of uniform size; great variation in the size of the grains is likely to result in irregular germination.

The weight of barleys varies from 50-56 lbs. per bushel. Light barleys, weighing from 50-52 lbs. per bushel, are best adapted to distillery purposes, as the malt obtained from them is, as a general rule, richer in diastase than that from heavier barleys, owing to their somewhat higher content of nitrogen.

Freshly harvested moist barley germinates badly. Barley intended for malting should contain from 12 to at most 14 per cent. of moisture. Other characteristics of good barley, such as fineness of skin, "mealiness," etc., to which the brewer attaches more or less significance, are not of great importance in the selection of grain for the distillery.

The most reliable information as to the suitability of a barley for malting is afforded by an actual germination test. This has, however,

the disadvantage of being a somewhat lengthy operation, three or four days at least being required.

2. MALT.

Green or air-dried malt is used to a comparatively small extent in Great Britain, and only in conjunction with the manufacture of patent-still spirit from maize, etc., where cheapness of production is the essential consideration. The flavour of pot-still whisky is to a large extent due to the use of cured malt and is influenced by the manner in which the malt is kilned.

The quality of green malt may in most cases be judged, after a certain amount of experience, from its external characteristics. Good green malt should be free from dirt and mould, and should possess an agreeable, fresh smell, neither musty nor acid.

In a properly modified green malt the acrospire and rootlets should be well developed, and should present a fresh and shiny appearance, not withered or wrinkled. In such malts the endosperm is mealy and friable, and of a uniform character.

Foreign seeds and dead corns should be as few in number as possible. Crushed corns, and corns with matted rootlets, should not be present, as their presence favours the formation of mould. Kiln-dried or cured malt intended for distilleries is dried at a low temperature, and should show a high content of diastase and protein.

1. The Determination of the Diastatic Power of Malt (Lintner Value).

The determination of the diastatic power is one of the most important tests that have to be applied to malt. The process is best carried out by A. R. Ling's method in accordance with the standard conditions proposed by the Malt Analysis Committee of the Institute of Brewing in 1906. The sample is prepared for analysis by grinding in a Seck mill set at 25, and 25 g. of the grist are extracted with 500 c.c. of distilled water for three hours at 70° F. (21° C.), the mixture being well stirred every half-hour. It is then filtered bright, and from 1-3 c.c. of the clear filtrate (according to the diastatic power of the sample) are added to 100 c.c. of 2 per cent. soluble starch solution in a 200 c.c. flask, the mixture being kept at 70° F. (21° C.) for one hour. 10 c.c. of *N*/10 sodium hydroxide solution are then added to stop further diastatic action, the liquid is cooled to 60° F. (15.5° C.), made up to 200 c.c. with distilled water at the same temperature, well shaken, and titrated against 5 c.c. of Fehling's solution, using ferrous thiocyanate as indicator. Further details respecting the method of titration, the preparation of the indicator, the preparation of soluble

starch, etc., are given in the report of the Malt Analysis Committee¹ of the Institute of Brewing.

The results are calculated by the following formula :—

$$A = \frac{1000}{XY}$$

in which A is the diastatic activity, X the number of cubic centimetres of malt extract contained in 100 c.c. of the fully diluted starch conversion liquid, and Y the number of cubic centimetres of the same liquid required for the reduction of 5 c.c. of Fehling's solution.

The diastatic power of English brewing malt is usually between 20° and 40° Lintner, while that of green malt may be as high as 100°-125°. The object of the distiller being to secure a high degree of diastatic action in his mash, the malt is dried at as low a temperature as possible, to avoid undue destruction of diastase, and a small proportion of green malt is often used in maize conversions at patent-still distilleries.

2. The Determination of the Liquefying Capacity of Malt.

A separate estimation of the liquefying power of malt for starch paste is not often required, but if desired may be determined by the following method (Lintner)² :—

25 g. of malt grist, ground in a Seck mill set at 25°, are extracted with 500 c.c. of distilled water for three hours at 21°, the mixture being well stirred every half-hour, and filtered. With green or lightly kilned malts it is often necessary to dilute the filtrate with 1 or 2 vols. of distilled water. 10 g. of potato starch are shaken up with 100 c.c. of water, and by means of a pipette with a wide opening portions of 10 c.c. are transferred to a series of test tubes, taking care that an even distribution of the starch granules is maintained by constant shaking. Quantities of 0.1, 0.2, 0.3, etc., c.c. of the malt extract are added to each of the tubes, and the contents of the tubes gelatinised by heating to 65° in a water-bath. The tubes are allowed to remain in the water-bath after gelatinisation for fifteen minutes, and are then heated in boiling water for ten minutes. They are then cooled to 17°.5. On inverting the tubes it will be found that when complete liquefaction of the starch has taken place the contents can easily be poured out, while if the amount of malt extract has been insufficient to effect liquefaction, the contents are still in a semi-solid gelatinous condition. The liquefying power of the malt used is taken to be 100 when 0.1 c.c. of the extract is sufficient to liquefy 10 c.c. of the 10 per cent. starch paste under the above conditions. If 0.2 c.c. are

¹ *J. Inst. Brewing*, 1906, 12, 1.

² *Z. ges. Brauw.*, 1903, p. 329.

required, the liquefying power of the malt is $\frac{100}{2} = 50$. Ordinary cured malts show when examined by this method liquefying powers between 40 and 75.

The degree of attenuation attained during the fermentation of the wort is dependent to a large extent on both the liquefying and saccharifying power of the malt. Green or lightly cured malt, possessing high liquefying and saccharifying power, will effect the most complete attenuation of the wash; malt with low liquefying power will not produce a satisfactory attenuation unless the saccharifying power is high.

The liquefying power of malt does not necessarily run parallel with the saccharifying power. The liquefying power is but slightly affected by drying at a low heat, while the saccharifying power is affected to a much greater degree.

3. The Estimation of Acidity.

The acid content of malt is dependent not only upon the quality of the barley employed, but also upon the way in which the malting has been carried out. The measurement of acidity may therefore be of considerable value in determining whether the process has been properly effected. An abnormally high acidity may be caused by too prolonged steeping and insufficient changing of the steep-water, by uncleanness of the malting floor, by negligent turning, and by too high a temperature during the malting process. Since the increase in acidity in the above cases is due chiefly to the activity of micro-organisms, it is nearly always associated with a mouldy, fusty smell, and the presence of moulds will be detected by microscopical examination.

To determine the acidity 50 g. of ground malt are digested with 300 c.c. of distilled water at 15° for three hours, and the extract filtered. It is then titrated with *N*/20 ammonium hydroxide solution, using litmus paper as an indicator. The acidity of malt is usually calculated as lactic acid, a mode of expression which is purely conventional as the greater part of the acidity is due to acid phosphates. The normal proportion of free acid is from 0.2 to 0.3 per cent., calculated as lactic acid, and it should not exceed 0.4 per cent.

4. The Estimation of Moisture.

About 5 g. of ground malt are accurately weighed out in a small shallow vessel, about 2 in. in diameter and 1 in. in depth, heated for five hours in a boiling water oven, allowed to cool in a desiccator, and re-weighed, the loss in weight being taken as the moisture-content and calculated as a percentage on the malt.

5. The Cold Water Extract.

For this determination 25 g. of ground malt are digested with 200 c.c. of distilled water containing 20 c.c. of $N/10$ ammonium hydroxide for three hours at 70° F. (21° C.), stirring about three or four times during this period. After filtering, the specific gravity of the clear filtrate is taken at 60° F. (15.5° C.), compared with water at the same temperature. The excess specific gravity over water (= 1000) divided by 3.86 and multiplied by 10 gives the cold water extract per cent.

Further information on the analysis of malt is given in the section on "Brewing Materials and Beer" (this Vol., pp. 809 *et seq.*).

III. THE EXAMINATION OF THE WORT.

1. The Iodine Test.

The progress of saccharification can be followed by testing the clear filtrate from the mash with a solution of iodine in potassium iodide. The sample is filtered through a folded filter, pouring back on to the filter the first runnings until a perfectly bright filtrate is obtained.

The iodine test depends upon the property possessed by starch and certain of its degradation products, of adsorbing iodine with the production of differently coloured substances. While starch itself gives a deep blue colour with iodine, the colorations obtained with the various dextrans vary from blue through violet to red, until with the lower degradation products no colour at all is produced.

The test may be carried out in the following manner:—1 part of iodine and 2 parts of potassium iodide are dissolved in distilled water, and the solution diluted until it is of a deep yellow colour. A few drops of the clear filtrate from the mash are added to about 10 c.c. of water in a test tube, and the liquids well mixed. The iodine solution is then added carefully, drop by drop, the tube being shaken after each addition, and the colour change observed. The first few drops of iodine solution are decolorised by the diluted wort, and if the saccharification has been complete, further addition of iodine will produce a distinct yellow coloration with no trace of red. If the saccharification is incomplete, the solution will become red, showing the presence of one or more of the higher dextrans, and further addition of iodine may produce a violet or even blue colour if any unaltered starch be present.

If the addition of the iodine solution is carefully carried out, it is possible to detect the presence of several starch degradation products in presence of each other, since the nearer the products are to maltose, the greater is their affinity for iodine.

In applying the iodine test care should be taken that the wort is previously cooled, and that the addition of iodine is continued until the yellow colour of the iodine solution is apparent in the liquid.

2. The Estimation of the Total Solids in Solution.

The total solids contained in a definite volume of the clear wort can be estimated with a near approach to accuracy by means of the specific gravity. This is ascertained in the laboratory by a specific gravity bottle, or pyknometer, and in distilleries by Bates' saccharometer, which is the official instrument used by the excise authorities. This saccharometer is designed to show degrees of gravity from 1000-1150, water being taken at 1000. It is constructed of brass, and is provided with five movable weights. The scale is graduated into thirty principal divisions divided into halves, and with the smallest weight attached, indicates degrees of gravity from 1000-1030. The other weights are marked 30, 60, 90, and 120, and when any of these is attached to the instrument, the number marked on the weight is added to the reading on the scale, and their sum added to 1000.

The approximate number of grams of solid matter contained in 100 c.c. of the wort is found by dividing the excess of gravity over 1000 by 4. Thus a wort of sp. gr. 1060 contains approximately

$$\frac{60}{4} = 15 \text{ g. of solids per 100 c.c.}$$

In British distilleries the gravity of patent-still worts varies from 1025-1035, and that of pot-still worts from 1045-1060.

On the Continent Balling's saccharometer is used almost exclusively in distilleries. The scale of this instrument is designed to give directly the parts by weight of cane sugar contained in 100 parts by weight of the liquid at a temperature of 17°.5. Although the indications of this instrument have reference to cane sugar, and not to the complicated mixture of fermentable and unfermentable substances present in wort, the difficulty of ascertaining the true percentages of extract in a wort from the specific gravity is so great that continental distillers consider it more satisfactory to refer the gravities to a solution of a pure substance of known composition. For the purposes of the distiller the indications thus obtained are sufficiently accurate, but it must be borne in mind that they are purely relative, and do not represent the absolute amount of solid matter present. Worts prepared from starchy materials contain, as a general rule, somewhat more solid matter than is indicated by Balling's saccharometer, while molasses worts contain less.

In using the saccharometer the usual precautions with regard to temperature, etc., must be observed.

3. The Estimation of "Apparent Maltose and Dextrin."

Malt worts contain a complicated mixture of malto-dextrins, maltose, dextrose, the pre-existent carbohydrates of the malt, proteins, and other nitrogenous matters and mineral constituents. A full analysis of malt worts is not often necessary, and if desired can be carried out according to the scheme given by Moritz and Morris in their *Text-book of the Science of Brewing*. In general it is sufficient to regard all the reducing sugar present as maltose, and to deduce the amount of dextrin present from the specific rotatory power after subtraction of the rotation due to maltose.

To carry out the estimation, the wort is boiled and filtered, and the percentage of solid matter found from the specific gravity as given above. The maltose is estimated by diluting 10 c.c. of the filtered wort to 250 c.c., and determining the amount of copper reduced by an aliquot part, either gravimetrically under the conditions laid down by Brown, Morris, and Millar,¹ or volumetrically by Ling and Rendle's method (pp. 564 and 824).

The specific rotatory power is determined in the clear wort, clarified if necessary with basic lead acetate or alumina cream. From the reading thus obtained is subtracted the rotation due to the maltose found, taking the $[\alpha]_D$ of maltose as 137° , and the remainder calculated to dextrin, on the assumption that the specific rotatory power of dextrin is 200° . In all-malt worts the amount of "apparent maltose" varies from 70-80 per cent., and the "apparent dextrin" from 4-10 per cent. of the total solid matter present, the high proportion of "apparent maltose" as compared with "apparent dextrin" being due to the presence of other sugars with a high cupric reducing power but a low specific rotation.

In patent-still worts when a comparatively small proportion of highly diastatic malt has been used to effect the conversion of a large quantity of starchy material, the actual proportion of maltose and dextrin can be approximately arrived at by the above methods. It has been shown by H. T. Brown and J. H. Millar² that when starch is hydrolysed by diastase, a well-defined resting stage occurs at which the liquid contains approximately 80.8 parts of maltose and 19.2 parts of dextrin, that is, a proportion of 4.2 parts of maltose to 1 part of dextrin. This proportion is, however, not always attained in practice.

In worts of this character the maltose and dextrin may be estimated from the copper reduction and specific rotatory power as given above, or the dextrin may be arrived at from the copper reduction after complete hydrolysis. In the latter method 10 g. of the clear wort

¹ *J. Chem. Soc.*, 1897, 71, 94.

² *J. Chem. Soc.*, 1899, 75, 315.

are diluted with 200 c.c. of water and heated for two and a half hours in a boiling water-bath with 15 c.c. of hydrochloric acid of sp. gr. 1.125. The dextrose present in the liquid, after neutralisation, is estimated in the ordinary manner. Slight errors may be caused in the gravimetric method by the presence in the wort of soluble phosphates, which cause a precipitate with Fehling's solution. Phosphates may be removed by the addition of a few drops of lead acetate solution to the diluted wort, and subsequent removal of the excess of lead by means of sodium sulphate solution.

The total quantity of dextrose found, calculated as a percentage on the original wort, gives the "dextrose value" of the substances present which are fermentable by yeast in the presence of active diastase. The dextrose due to maltose is found by multiplying the maltose by the factor 1.053, and the amount thus found is subtracted from the total dextrose to ascertain the dextrose due to dextrin. This multiplied by 0.9 gives the dextrin contained in the wort.

The following example will illustrate the method of calculation :—

	Per cent.
Total solid matter (by saccharometer)	10.95
Total dextrose	10.56
Maltose	7.67
Dextrin $(10.56 - [7.67 \times 1.053]) \times 0.9$	= 2.24
Content of fermentable substances	$7.67 + 2.24 = 9.91$
Content of non-fermentable substances	$10.95 - 9.91 = 1.04$

Ratio of maltose to dextrin = 3.4 : 1.

On the Continent considerable stress is laid upon the quotient of purity of a wort, that is, the percentage of fermentable matter present in 100 g. of total wort solids as found by the saccharometer.

When the percentage of fermentable matter is reckoned in terms of maltose and dextrin, the resulting percentage is called the "true quotient" of the wort, and when in terms of total dextrose obtainable by hydrolysis it is called the "dextrose quotient."

The dextrose quotient may be usefully employed in the calculation of the probable yield of alcohol on fermentation, while the true quotient is a measure of the unfermentable matter present.

In the sample given above the true quotient is :—

$$Q = \frac{(7.67 + 2.24) \times 100}{10.95} = 90.5$$

and the dextrose quotient :—

$$Q = \frac{10.56 \times 100}{10.95} = 96.4$$

Maercker gives the following dextrose quotients for potato and maize worts:—

	Minimum.	Mean.	Maximum.
Worts from potatoes very rich in starch .	86	90	92
Worts from potatoes fairly rich in starch .	83	85	86
Worts from average potatoes .	80	82	85
Maize worts	97.99	...

4. The Acidity.

Very small quantities of volatile acids are capable of affecting adversely the process of saccharification by diastase. A determination of the acidity of the wort should be made before it is set for fermentation. It is also advisable to estimate the acidity after pitching, so that the increase of acidity during the course of fermentation may be controlled. Within certain limits the lower the initial acidity of the wort, and the smaller the increase of acidity during fermentation, the more regular will be the fermentation and the higher the yield of alcohol.

The acidity is measured by titration with $N/10$ ammonium hydroxide, using litmus paper as indicator. 20 c.c. of the wort should not require more than 6 c.c. of $N/10$ ammonium hydroxide for neutralisation, 2-4 c.c. being the usual amount.

IV. THE EXAMINATION OF THE FERMENTED WORT (WASH).

The content of the wash back should be thoroughly and completely mixed before taking a sample, and the sample should be filtered completely clear, with precautions against loss by evaporation.

1. The Presence of Diastase.

In the process of saccharification, the conversion of starch into maltose is, as is well known, by no means complete. A further hydrolysis of undissolved starch and of dextrin is effected during fermentation by the diastase present in the wort. It is therefore absolutely necessary that a sufficient quantity of diastase should be present in the liquid up to the end of the fermentation process. If defective fermentation cannot be traced to other causes, the wash should be tested for the presence of diastase.

A simple test for diastase is that of Schönbein, as modified by Lintner, which depends upon the blue coloration given by the enzyme with guaiacum resin and hydrogen peroxide. A small fragment of guaiacum resin is dissolved in 1-2 c.c. of absolute alcohol in a test tube, the solution always being freshly prepared. A few drops of hydrogen peroxide are added, and a further addition of alcohol is made until

the liquid is clear. If a liquid containing diastase is added, drop by drop, to this solution, an intense blue coloration is obtained immediately. Other enzymes such as chymosin (the enzyme of rennet), pepsin, invertase, etc., do not give this reaction.

A more reliable method for the detection of diastase is afforded by the use of soluble starch. The test is conveniently carried out as follows:—A 2 per cent. solution of soluble starch in distilled water is prepared, and 20 c.c. added to each of six test tubes. To the contents of the tubes are added 0.25, 0.5, 0.75, 1.0, 1.25, and 1.50 c.c. of the filtered wash, the tubes being then placed in a water-bath at 60° for one hour, cooled and treated with 0.5 c.c. of a dilute solution of iodine in potassium iodide. An absence of coloration in the tubes to which 0.75-1.25 c.c. of filtered wash has been added indicates that a sufficient amount of diastase has been present during the fermentation. If, on the other hand, the tube containing 1.5 c.c. of filtered wash is the only one in which no coloration is observed, an undue inhibition of diastatic action during fermentation is indicated.

The chief causes of such inhibition are too high a mashing temperature, and excessive development of acidity during fermentation. The latter may be due to the use of raw materials of inferior quality, or to the use of impure yeast, and to infection of the wort by acid-producing micro-organisms.

2. Microscopic Examination.

A microscopic examination should be carried out on the unfiltered wash, which is diluted for this purpose as required. The appearance of the yeast cells should be noted, and any foreign micro-organisms looked for which may be prejudicial to fermentation. Inasmuch as the correct interpretation of the phenomena observed requires not only an intimate knowledge of microscopical work in general, but also a special knowledge of mycology and bacteriology, the reader is referred to the standard works on these subjects.

3. The Degree of Fermentation. "Attenuation."

The difference between the original gravity of the wort and the lowest gravity after fermentation is called "attenuation," and the aim of the distiller is to get as high an attenuation of his wash as possible. A fully attenuated distillery wash shows approximately the same specific gravity as that of water, the effect of the alcohol present in reducing the gravity being compensated for by the residual non-fermentable substances in solution. In Great Britain an Excise charge is raised upon the "attenuation" of the wort, upon the assumption that every 5° of attenuation in 100 gals. of wash corresponds to the production of 1 gal. of proof spirit. Thus if the original gravity of the wort were

1050, and after fermentation were finished the gravity had sunk to 1000, the Excise charge would be based upon the assumption that the wash contained 10 per cent. of spirit at proof strength. As a matter of fact, the yield of spirit in pot-still distilleries usually exceeds that calculated on the attenuation charge by at least 11 per cent., and corresponds to the production of 1 gal. of proof spirit for every $4\frac{1}{2}^\circ$ of attenuation in 100 gals. of wash. In patent-still operations the excess of the actual net yield over the attenuation charge is about 7 per cent. Inasmuch as the gravity of the wash is influenced on the one hand by the amount of alcohol present, and on the other hand by the amount of unfermented matter remaining, and also to a smaller extent by the secondary products of fermentation, the indications afforded by a measurement of the attenuation are purely comparative, and must be supplemented by an estimation of the alcohol present, and of the maltose and dextrin remaining in the wash. By distilling off the alcohol from 100 c.c. of the wash and making up the residue to the original volume with distilled water (*cf.* the "original gravity" method given in the section on "Brewing Materials and Beer," p. 832), the approximate content of the wash in unfermentable matter can be ascertained. A polarimetric examination of the filtered wash is often of value in ascertaining the degree of attenuation, the rotation of a fully fermented wash being practically nil.

4. The Estimation of Maltose and Dextrin.

For this estimation 200 c.c. of the filtered wash are treated with 5-6 c.c. of a saturated solution of lead acetate, the solution made up to 250 c.c., well mixed, and filtered; 200 c.c. of the filtrate are treated with dilute sodium sulphate solution in slight excess to remove excess of lead, made up again to 250 c.c., and filtered.

For the determination of maltose 100 c.c. of the filtrate, free from lead, are diluted to 200 c.c., and the copper reduction estimated on 25 c.c. (corresponding to 8 c.c. of the original solution). For the estimation of total carbohydrates, 100 c.c. of the lead-free filtrate are diluted to 200 c.c. and hydrolysed by heating with 10 c.c. of hydrochloric acid (sp. gr. 1.125) for two and a half hours in a boiling water-bath. The liquid is then almost neutralised with sodium hydroxide solution, made up to 400 c.c., and filtered. A copper reduction is carried out on 125 c.c. of the filtrate (corresponding to 4 c.c. of the original sample). The calculation of the quantities of maltose or dextrin present is carried out as given on p. 703.

Under normal conditions the maltose-content of the fermented wash is usually from 0.5-0.6 per cent., and the dextrin-content from 0.6-0.9 per cent. A considerably higher content of maltose may arise from the

use of a defective yeast, or from the employment of too high a temperature in fermentation with consequent development of excessive acidity in the wash. In such cases valuable information may often be obtained from a microscopical examination. The ratio of maltose to dextrin in the fermented wash will indicate with certainty whether incomplete fermentation is to be attributed to a deficiency in active diastase. If the amount of dextrin present is more than double that of the maltose, defective diastatic action is indicated; under normal conditions the proportion of maltose to dextrin is from 1 : 1.25 to 1 : 1.5.

5. Acidity.

This determination is carried out in the same manner as for sweet worts. The difference between the acidity of the wort immediately after pitching and of the fermented wash represents the increase of acidity during fermentation. Under normal conditions the increase of acidity should not be more than the equivalent of 2 c.c. of *N*/10 acid per 20 c.c. of the wash (=0.09 per cent. of lactic acid). The total acidity of fully fermented wash ranges from 0.3 to 0.4 per cent., calculated as lactic acid.

6. Estimation of Alcohol.

This is usually carried out on the filtered wash. The carbon dioxide is first removed by pouring the liquid several times from one vessel to another. 100 c.c. of the filtrate at a temperature of 15° are introduced into a distilling flask (the "original gravity" apparatus is generally used), neutralised and diluted with 40 c.c. of water. The liquid is distilled until 80 c.c. have passed over, when the distillate is made up to 100 c.c. at 15° and the specific gravity determined. The amount of alcohol is found by reference to Tables (*cf.* p. 711).

Patent-still washes usually contain from 5-8 per cent. of proof spirit, while pot-still washes contain from 8-12 per cent.

The amount of alcohol found by distillation of the wash in the laboratory is always somewhat in excess of that obtained in practice, since it is impossible to prevent a slight loss of alcohol in the distillery, even with the most perfect forms of still, and at the same time the separation of the fusel oil is more efficiently carried out on the large scale than is possible in a laboratory distillation experiment.

Märcker gives the following estimate of the total loss of material in practice from various causes, calculated as percentages on the starch originally present:—

	Per cent. of original Starch.		
Loss due to incomplete conversion	0.5	to	2.0
Loss due to incomplete fermentation	4.0	„	7.0
Loss due to formation of secondary products, evaporation, etc.	7.2	„	11.0
Total loss	11.7	„	20.0

This corresponds to an actual recovery of from 80-88.3 per cent. of the starch in the form of alcohol.

7. The Total Nitrogen and the Soluble Nitrogen.

In ordinary distilling practice a knowledge of the amount of nitrogen present in the soluble form before and after fermentation is not often of value, being of more importance where the manufacture of pressed yeast is the primary consideration. The nitrogen removed from solution during the growth of the yeast may be found by estimating the total nitrogen present in the filtrates from the sweet wort and fermented wash respectively. The amount of nitrogen thus removed varies considerably with different varieties of yeast and under different conditions of growth. According to Balling, a removal of 1 kg. of nitrogen corresponds to the production of 51.2 kg. of pressed yeast.

In following the course of the fermentation, an examination of the wash while fermentation is still active may often be necessary. In order to inhibit further action of the yeast after the sample has been taken, 10 c.c. of a 1 per cent. mercuric chloride solution may be added to 1 litre of the sample, the increase of volume thus caused being taken into account when calculating the results.

8. The Examination of Fermented Molasses Washes.

The examination differs in the following points from that of washes prepared from starchy materials. If the fermentation is abnormal or incomplete, the sample should be tested for the presence of free nitrous acid and volatile fatty acids (see p. 694). Defective fermentation may also be due to too high a content of soluble salts, or to excessive acidity in the original wort. The yeast in such cases is found to be badly developed and to consist of a large proportion of dead cells, while great numbers of bacteria may be present. The ash soluble in water may be determined in 10 c.c. of the filtered wash by evaporating to dryness in a platinum dish, and igniting the residue gently at a low heat until a white ash is obtained. The ash is then extracted with water, and the residue washed with water on a filter until the washings no longer give an alkaline reaction. The clear filtrate is evaporated to dryness in a weighed platinum dish, and heated in a steam-oven to constant weight.

According to H. F. Bauer, the soluble ash of molasses washes should not greatly exceed 3 per cent.

The only residual sugar present in fermented molasses washes is lævulose, the other product of inversion, dextrose, being the more easily fermented of the two. Under normal conditions, not more than 0.05-

0.1 per cent. of lævulose remains unfermented. For the estimation of the lævulose the wash should be suitably diluted and clarified with basic lead acetate, the excess of lead being removed by means of sodium sulphate. A copper estimation is carried out on an aliquot part of the filtrate.

V. ALCOHOLOMETRY.

The estimation of alcohol in commercial spirits is effected by the determination of the specific gravity. There is some doubt as to the correct specific gravity of pure absolute alcohol at 60°/60° F., which is the temperature adopted for alcoholometry in Great Britain. It is probable that the true specific gravity at this temperature is 0.79394, according to the work of Mendeléef in 1865, S. Young¹ and P. Klason and E. Norlin.² Tralles in 1811, in an investigation carried out for the Prussian Government, found the specific gravity of absolute alcohol at 60° F./60° F. to be 0.7946, but it is probable that this value was somewhat too high. Fownes and Drinkwater in 1847, working independently, found the values 0.7938 and 0.79381 respectively, and E. R. Squibb³ in 1884 prepared alcohol of as low a gravity as 0.7935; but it is possible that Squibb's alcohol contained traces of ether.

The Tables of the British Excise are based upon the original determinations of Blagden and Gilpin published in the years 1790-94, and the high degree of accuracy obtained in these determinations has been repeatedly confirmed by subsequent observers, more especially by Drinkwater. Stevenson's Tables, given in shortened form below, are based upon those of Blagden and Gilpin. Hehner's Tables are based upon determinations made by Fownes in 1847, and differ slightly at certain points from those of Stevenson.

The Tables in use in most Continental countries and in America are based upon those of Tralles, which agree very closely with the earlier ones of Blagden and Gilpin.

For Excise purposes the content of alcohol in any liquid is always reckoned in terms of "proof spirit." Proof spirit is defined by Act of Parliament, 58 Geo. III., c. 28, as alcohol of such a strength that at a temperature of 51° F. a given volume weighs $\frac{1\frac{2}{3}}{1}$ of the weight of an equal volume of distilled water. The temperature of the water is not specifically stated, but is taken as being 51° F. 100 vols. of an alcoholic liquid of strength "25 over proof" contain alcohol equivalent to $100 + 25 = 125$ vols. of proof spirit, while 100 vols. of an alcoholic liquid of strength 25 under proof are equivalent to $100 - 25$ or

¹ *J. Chem. Soc.*, 1902, 81, 717.

² *Arkiv f. Kemi.*, 1906, 2 [3], No. 24; *Chem. Zentr.*, 1906, II., 1480.

³ *Ephemeris*, ii., p. 522; *Pharm. J.*, 1884-85, [3] 15, 22.

75 vols. of proof spirit. These strengths may also be expressed as 125 per cent. and 75 per cent. of proof spirit respectively.

The most recent work on the subject has shown that proof spirit contains 49.277 per cent. by weight and 57.029 per cent. by volume of absolute alcohol. The most accurate Tables at present available give the amount of alcohol in proof spirit as 49.25 per cent. by weight and 57.05 per cent. by volume; the differences from the above values are, for most purposes, negligible.

For the determination of the specific gravity of mixtures of alcohol and water, the official instrument in Great Britain is *Sikes' Hydrometer*. This hydrometer consists of a hollow brass ball usually 1.5-1.6 in. in diameter, to opposite poles of which are fixed the stems. The lower of the stems is the shorter, being about 1.7 ins. long, and is weighted so that the instrument floats in an upright position. The upper stem is usually about $3\frac{1}{2}$ in. long, 0.2 in. wide, and 0.1 in. thick. It is graduated upon both its flat sides, the highest mark being 0 and the lowest 10. The ten principal divisions are each subdivided into tenths, so that the scale bears fifty divisions in all. There are nine detachable weights with the instrument, which slip over the lower stem. They are numbered 10, 20, . . . 90, and in this way the instrument is capable of measuring a considerable range of specific gravities. A Table is supplied with the hydrometer giving the strengths of alcohol corresponding to the readings on the stem when different weights are attached. The accuracy of a Sikes' hydrometer may be tested in the following manner:—

1. Applied to spirits at proof strength, at 51° F., the instrument should float at the proof-mark, when the weight 60 is on the stem. This mark is the fourth subdivisional reading from the zero point, or the indication 0.8. The total indication at the proof-mark is therefore 60.8.
2. In distilled water at 51° F., with the brass cap (supplied with the instrument) on the stem top, and the weight 60 attached, the instrument will float at the proof-mark, 60.8.
3. In distilled water at 51° F., with the weight 90 attached, the hydrometer will float at the indication 10, giving a full indication of 100.

The existence of certain errors in Sikes' system has been pointed out by B. Derham¹ and others, and several alternative systems have been suggested.

In the laboratory, the specific gravity of mixtures of alcohol and water is determined by means of the pycnometer or specific gravity bottle. The volume of the latter is usually 50 c.c., but in all cases the

¹ *J. Soc. Chem. Ind.*, 1888, 7, 276, 819.

Table 57.

Table of Specific Gravities of Mixtures of Alcohol and Water.
(T. Stevenson.)

Specific gravity at $\frac{60^{\circ}}{60^{\circ}}$ F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.	Specific gravity at $\frac{60^{\circ}}{60^{\circ}}$ F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.
0.7938	100.00	100.00	175.25	0.8440	81.65	86.80	152.1
0.7940	99.95	99.95	175.2	0.8450	81.20	86.50	151.5
0.7950	99.60	99.75	174.8	0.8460	80.80	86.15	150.9
0.7960	99.30	99.55	174.4	0.8470	80.45	85.90	150.3
0.7970	98.95	99.40	174.1	0.8480	80.05	85.50	149.7
0.7980	98.65	99.20	173.8	0.8490	79.60	85.15	149.1
0.7990	98.35	99.00	173.5	0.8500	79.20	84.80	148.6
0.8000	98.00	98.75	173.1	0.8510	78.80	84.45	148.0
0.8010	97.70	98.55	172.7	0.8520	78.40	84.15	147.4
0.8020	97.35	98.40	172.4	0.8530	78.00	83.80	146.7
0.8030	97.05	98.15	172.0	0.8540	77.55	83.45	146.2
0.8040	96.70	97.95	171.6	0.8550	77.15	83.15	145.6
0.8050	96.35	97.70	171.2	0.8560	76.70	82.75	145.0
0.8060	96.05	97.50	170.8	0.8570	76.30	82.40	144.4
0.8070	95.70	97.25	170.4	0.8580	75.85	82.00	143.8
0.8080	95.30	97.05	170.0	0.8590	75.50	81.70	143.2
0.8090	94.95	96.80	169.6	0.8600	75.10	81.35	142.6
0.8100	94.60	96.55	169.2	0.8610	74.70	81.00	141.9
0.8110	94.30	96.35	168.8	0.8620	74.25	80.60	141.3
0.8120	93.95	96.10	168.4	0.8630	73.80	80.25	140.7
0.8130	93.55	95.80	167.9	0.8640	73.45	79.95	140.1
0.8140	93.20	95.50	167.4	0.8650	73.00	79.55	139.4
0.8150	92.80	95.25	167.0	0.8660	72.55	79.15	138.8
0.8160	92.45	95.00	166.5	0.8670	72.20	78.75	138.1
0.8170	92.05	94.75	166.1	0.8680	71.75	78.45	137.4
0.8180	91.70	94.50	165.6	0.8690	71.30	78.10	136.6
0.8190	91.35	94.25	165.1	0.8700	70.85	77.70	136.1
0.8200	90.95	94.00	164.7	0.8710	70.50	77.35	135.6
0.8210	90.65	93.75	164.3	0.8720	70.05	76.95	134.9
0.8220	90.25	93.50	163.9	0.8730	69.65	76.60	134.3
0.8230	89.90	93.25	163.4	0.8740	69.20	76.15	133.5
0.8240	89.50	92.90	162.8	0.8750	68.80	75.80	132.9
0.8250	89.05	92.55	162.2	0.8760	68.40	75.45	132.2
0.8260	88.65	92.30	161.7	0.8770	67.95	75.10	131.6
0.8270	88.30	92.00	161.2	0.8780	67.55	74.70	130.9
0.8280	87.90	91.70	160.7	0.8790	67.05	74.30	130.2
0.8290	87.50	91.40	160.2	0.8800	66.65	73.90	129.6
0.8300	87.15	91.10	159.7	0.8810	66.25	73.50	128.9
0.8310	86.75	90.85	159.1	0.8820	65.80	73.15	128.2
0.8320	86.35	90.55	158.6	0.8830	65.40	72.75	127.5
0.8330	85.95	90.25	158.1	0.8840	65.00	72.35	126.8
0.8340	85.60	89.95	157.6	0.8850	64.55	71.90	126.0
0.8350	85.20	89.60	157.1	0.8860	64.15	71.60	125.4
0.8360	84.80	89.30	156.5	0.8870	63.70	71.20	124.7
0.8370	84.40	89.00	156.0	0.8880	63.25	70.75	124.0
0.8380	84.00	88.65	155.4	0.8890	62.85	70.35	123.3
0.8390	83.60	88.35	154.9	0.8900	62.45	69.95	122.6
0.8400	83.20	88.05	154.3	0.8910	62.00	69.60	121.9
0.8410	82.80	87.75	153.8	0.8920	61.55	69.15	121.1
0.8420	82.45	87.45	153.2	0.8930	61.10	68.75	120.5
0.8430	82.00	87.10	152.7	0.8940	60.70	68.35	119.8

Table 57—*continued.*

Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.	Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.
0.8950	60.30	68.00	119.2	0.9480	35.50	42.40	74.3
0.8960	59.85	67.55	118.4	0.9490	35.00	41.85	73.3
0.8970	59.35	67.05	117.5	0.9500	34.40	41.20	72.2
0.8980	58.95	66.65	116.8	0.9510	33.85	40.55	71.0
0.8990	58.55	66.30	116.2	0.9520	33.30	39.90	70.0
0.9000	58.05	65.80	115.4	0.9530	32.70	39.20	68.7
0.9010	57.60	65.35	114.6	0.9540	32.15	38.60	67.6
0.9020	57.20	65.00	113.9	0.9550	31.55	37.95	66.5
0.9030	56.75	64.55	113.1	0.9560	31.00	37.35	65.4
0.9040	56.35	64.10	112.3	0.9570	30.35	36.55	64.1
0.9050	55.90	63.70	111.6	0.9580	29.70	35.85	62.8
0.9060	55.45	63.30	110.9	0.9590	29.10	35.10	61.6
0.9070	54.95	62.80	110.0	0.9600	28.45	34.40	60.3
0.9080	54.55	62.60	109.3	0.9610	27.80	33.60	59.0
0.9090	54.10	61.95	108.5	0.9620	27.15	32.90	57.6
0.9100	53.65	61.50	107.8	0.9630	26.45	32.05	56.2
0.9110	53.25	61.05	107.0	0.9640	25.70	31.20	54.7
0.9120	52.80	60.65	106.3	0.9650	25.00	30.40	53.3
0.9130	52.35	60.15	105.5	0.9660	24.25	29.55	51.8
0.9140	51.90	59.75	104.7	0.9670	23.50	28.65	50.2
0.9150	51.45	59.30	103.9	0.9680	22.75	27.75	48.6
0.9160	51.00	58.85	103.1	0.9690	21.95	26.85	46.9
0.9170	50.55	58.40	102.3	0.9700	21.10	25.75	45.2
0.9180	50.10	57.90	101.5	0.9710	20.35	24.90	43.6
0.9190	49.65	57.40	100.6	0.9720	19.55	23.90	42.0
0.9198	49.25	57.05	100.0	0.9730	18.80	23.05	40.5
0.9200	49.15	56.95	99.8	0.9740	17.90	21.95	38.5
0.9210	48.65	56.50	99.0	0.9750	17.10	21.00	36.8
0.9220	48.25	56.05	98.2	0.9760	16.30	20.00	35.1
0.9230	47.80	55.55	97.4	0.9770	15.45	19.00	33.3
0.9240	47.30	55.10	96.5	0.9780	14.65	18.00	31.6
0.9250	46.90	54.60	95.6	0.9790	13.80	17.00	29.8
0.9260	46.40	54.10	94.8	0.9800	13.00	16.00	28.0
0.9270	45.95	53.65	94.1	0.9810	12.25	15.10	26.5
0.9280	45.50	53.15	93.2	0.9820	11.45	14.10	24.7
0.9290	45.00	52.70	92.3	0.9830	10.65	13.20	23.1
0.9300	44.55	52.15	91.4	0.9840	9.90	12.35	21.5
0.9310	44.10	51.70	90.6	0.9850	9.20	11.40	20.0
0.9320	43.60	51.20	89.8	0.9860	8.50	10.55	18.4
0.9330	43.15	50.70	88.9	0.9870	7.80	9.65	16.9
0.9340	42.60	50.15	87.9	0.9880	7.10	8.80	15.5
0.9350	42.15	49.65	87.0	0.9890	6.40	8.00	14.1
0.9360	41.65	49.10	86.1	0.9900	5.75	7.15	12.6
0.9370	41.15	48.60	85.1	0.9910	5.15	6.40	11.2
0.9380	40.65	48.05	84.1	0.9920	4.50	5.65	9.9
0.9390	40.15	47.50	83.3	0.9930	3.90	4.90	8.6
0.9400	39.70	47.00	82.4	0.9940	3.30	4.15	7.2
0.9410	39.15	46.40	81.4	0.9950	2.75	3.50	6.1
0.9420	38.65	45.85	80.4	0.9960	2.15	2.70	4.9
0.9430	38.20	45.40	79.5	0.9970	1.60	2.00	3.5
0.9440	37.65	44.75	78.4	0.9980	1.05	1.30	2.4
0.9450	37.10	44.15	77.6	0.9990	0.55	0.65	1.2
0.9460	36.55	43.60	76.4	0.9999	0.05	0.05	0.1
0.9470	36.05	43.00	75.4				

actual weight of water contained in the bottle at the particular temperature of experiment must be ascertained.

The following equations may be used for calculating the percentage of alcohol by weight and volume from the percentage of proof spirit, and *vice versa*, where :—

W = percentage of alcohol by weight ; V = percentage of alcohol by volume ; P = percentage of proof spirit ; and D = specific gravity :—

$$V = P \times 0.5706. \quad V = \frac{WD}{0.7938} = WD \times 1.26.$$

$$P = \frac{V}{0.5706} = V \times 1.7525. \quad D = WD \times 2.208.$$

$$W = \frac{P}{D \times 2.208}. \quad W = \frac{V \times 0.7938}{D}.$$

In France, the proportion of alcohol in an alcoholic liquid is frequently estimated from the boiling point of the liquid. Several forms of apparatus have been designed for the purpose, being designated "ebullioscopes" or "ebulliometers." It is claimed that these instruments give results comparable in accuracy with those obtained from the specific gravity.¹ Other methods depending on the freezing point, on the rate of dilatation by heat, on the vapour tension, and on the surface tension of mixtures of alcohol and water have been proposed, but none of these methods has come into general use in Great Britain, possibly on account of the complexity of the apparatus required and, in general, the lower degree of accuracy attainable by them.

The same may be said of the Zeiss immersion refractometer as applied to the analysis of alcoholic distillates. B. Wagner and F. Schultze² have published a set of Tables for use with this instrument, but it is necessary to maintain an absolutely constant temperature during the observations if reliable results are to be obtained.

VI. DENATURED ALCOHOL.

The materials used for denaturing alcohol in Great Britain are wood naphtha and mineral naphtha (petroleum), although other substances may be used by manufacturers subject to certain Excise restrictions. There are two kinds of methylated spirit :—industrial methylated spirit, which contains not less than 5 per cent. of approved wood naphtha or other substance or combination of substances approved by the Excise authorities ; and mineralised methylated spirit, containing not less than 10 per cent. by volume of approved wood naphtha together with not less than 0.375 per cent. of approved mineral naphtha (petroleum of sp. gr. not less than 0.800).

¹ Cf. J. C. Cain, *Chem. News*, 1914, 109, 37.

² *Z. anal. Chem.*, 1907, 46, 508.

Under Section 8 of the Finance Act, 1902, an alternative to the use of methylated spirit was opened to manufacturers, under which spirits may be employed after being subjected to some special process of denaturing, appropriate to the particular industry, or possibly even in a pure state without payment of duty, under special licence from the Commissioners of Inland Revenue.

The provisions of the 1902 Act are taken advantage of in, *e.g.*, the manufacture of fulminate of mercury, where the alcohol used is denatured with 10 per cent. of the spirit recovered in the process of manufacture together with 0.025 per cent. of bone oil; in the production of tolidine and benzidine, where the denaturant consists of 2 per cent. of nitrotoluene; and in the manufacture of xylonite, where the pure alcohol is treated with camphor. These are, however, isolated instances, and for practical purposes the only denaturants of importance are wood naphtha and petroleum.

In Germany there are two grades of denatured alcohol—"completely denatured" and "incompletely denatured." The processes authorised for "complete denaturing" are two, viz.:—

- (a) An admixture with every 100 litres of spirit of $2\frac{1}{2}$ litres of a mixture containing 4 parts of wood naphtha and 1 part of pyridine bases (to this mixture 50 g. of lavender or rosemary oil may be added optionally, to counteract the smell of the pyridine bases).
- (b) An admixture with the spirit of half the quantity (viz., $1\frac{1}{4}$ litres per 100 litres of spirit) of the above denaturing mixture, together with an addition of $\frac{1}{4}$ litre of a solution of methyl violet and of benzene in quantities that may range from 2-20 litres to every 100 litres of spirit.

The processes authorised for "incomplete denaturing" are numerous. They consist—

- (a) Of two alternative processes of general application, viz.:—The addition to every 100 litres of spirit of either 5 litres of wood naphtha, or of $\frac{1}{2}$ litre of pyridine bases.
- (b) Of numerous processes of special application. Of these the processes applicable to the most numerous and most important industries, including coal tar colours and chemical preparations, are the four alternatives of:—

An addition to every 100 litres of spirit of—

- 10 litres of sulphuric ether,
- or 1 litre of benzene,
- or $\frac{1}{2}$ litre of turpentine,
- or 0.025 litre of animal oil.

Somewhat similar regulations are in force in France, Russia, Switzerland, and other European countries.

A.—THE EXAMINATION OF WOOD NAPHTHA.

Wood naphtha used for methylation in Great Britain is required to conform to the following tests:—

- (a) Not more than 30 c.c. of the naphtha should be required to decolorise a solution containing 0.5 g. of bromine.
- (b) The naphtha, which must be neutral or only slightly alkaline to litmus, should require at least 5 c.c. of decinormal acid to neutralise 25 c.c. of the spirit when methyl orange is used as the indicator.

It should contain:—

- (a) Not less than 72 per cent. by volume of methyl alcohol.
- (b) Not more than 12 g. per 100 c.c. of acetone, aldehydes, and higher ketones, estimated as "acetone" by the formation of iodoform according to J. Messinger's method.
- (c) Not more than 3 g. per 100 c.c. of esters, estimated as methyl acetate by hydrolysis.

In the Government Laboratory the above tests are conducted in the following manner:—

1. Bromine Decolorisation.

A standard bromine solution is made by dissolving 12.406 g. of potassium bromide and 3.481 g. of potassium bromate in a litre of boiled, distilled water. 50 c.c. of this standard solution (=0.5 g. of bromine) are placed in a flask of about 200 c.c. capacity having a well-ground stopper; to this is added 10 c.c. of dilute sulphuric acid (1 in 4), and the whole shaken gently. After standing for a few minutes the wood naphtha is slowly run from a burette into the clear, brown solution of bromine until the latter is completely decolorised. Not more than 30 c.c. of the wood naphtha should be required for this purpose.

2. The Methyl Orange Alkalinity Test.

The naphtha should be faintly acid to phenolphthalein, slightly alkaline or neutral, rarely acid to litmus, and always alkaline to methyl orange. To carry out the test, 25 c.c. of the wood naphtha are placed in each of two beakers, and titrated with decinormal acid, using in the one case a few drops of litmus solution, and in the other of a solution of methyl orange, as indicator. With litmus, usually 0.1-0.2 c.c. of decinormal acid is required for neutralisation; with methyl orange, the total alkalinity should be greater, at least 5 or 6 c.c. of decinormal acid being required for neutralisation.

The total alkalinity, less that given with litmus, is the "methyl orange alkalinity," and for the 25 c.c. of wood spirit, should not be less than is required to neutralise 5 c.c. of decinormal acid.

3. The Estimation of Methyl Alcohol.

For this estimation 22 g. of coarsely powdered iodine, and 5 c.c. of distilled water, are placed in a small flask and cooled by immersion in ice-cold water. Then 5 c.c. of the wood spirit (60.0 over proof) are added, the flask corked, the contents gently shaken, and allowed to remain in the ice-cold bath for ten to fifteen minutes.

When well cooled, 2 g. of red phosphorus are added to the mixture of spirit and iodine in the flask and the latter is immediately attached to a reflux condenser. The reaction soon commences, and must be moderated by dipping the flask into a cold water-bath. (Spirit may be lost if the action is too violent.) After about fifteen to twenty minutes, when all action appears to have ceased, the water-bath under the flask is gradually heated to a temperature of about 75° , and the flask, with occasional shaking, allowed to remain at this temperature for about fifteen to twenty minutes. The source of heat is then removed, and the apparatus left for an hour until it has cooled, when the condenser is reversed, and the methyl iodide slowly distilled off, first at a low temperature, the bath being allowed to boil towards the end of the operation only. The end of the condenser dips into water in a measuring tube, and the iodide is collected under water and measured at a temperature of $15^{\circ}5$.

The percentage by volume of methyl alcohol in the original sample is found by the following formula:—

$$\frac{\text{c.c. methyl iodide found} \times 0.647 \times 100}{\text{c.c. wood spirit taken}} = \text{percentage by volume of methyl alcohol};$$

or, when 5 c.c. of spirit are taken:—

$$\text{c.c. methyl iodide} \times 12.94 = \text{percentage of methyl alcohol by volume.}$$

Esters, acetates, etc., also yield methyl iodide by this process, and from the percentage of methyl alcohol calculated as above, an amount equivalent to the percentage of these substances present must be deducted. Practically, however, methyl acetate is the only compound usually found in sufficient quantity materially to affect the result. The number of grams of methyl acetate for 100 c.c. of spirit multiplied by 0.5405 gives the equivalent of methyl alcohol to be deducted from the total percentage by volume calculated from the methyl iodide found.

4. The Estimation of Acetone.

To estimate the content of acetone, 25 c.c. of normal sodium hydroxide solution are placed in a flask similar to those used in the

bromine reaction. To this is added 0.5 c.c. of the naphtha. The mixture is well shaken, and allowed to stand for five to ten minutes. Into it, from a burette, $N/5$ iodine solution is run slowly, drop by drop, vigorously shaking all the time until the upper portion of the solution, on standing for a minute, becomes quite clear. A few cubic centimetres more of $N/5$ iodine solution are added, as to get concordant results an excess of at least 25 per cent. of the iodine required must be present. After shaking, the mixture is allowed to stand for ten to fifteen minutes, and then 25 c.c. of normal sulphuric acid are added. The excess of iodine is liberated, titrated with $N/10$ sodium thiosulphate and starch, and half the number of cubic centimetres of thiosulphate solution used are deducted from the total number of cubic centimetres of iodine solution used. The difference gives the amount of acetone by weight in the naphtha according to the equation :—

$$\text{c.c. } N/5 \text{ iodine solution required} \times 0.3867 = \text{g. of acetone per 100 c.c. of wood naphtha.}$$

This includes, as acetone, any aldehydes, etc., capable of yielding iodoform by this reaction.

If the quantity of "acetone" is excessive, a smaller quantity of the spirit is taken, or 10 c.c. are diluted with 10 c.c. of methyl alcohol, free from acetone, and 0.5 c.c. of the mixture is used.

5. The Estimation of Esters.

5 c.c. of the wood naphtha are run into a silver pressure flask of about 150 c.c. capacity, together with 20 c.c. of recently boiled, distilled water; 10 c.c. of normal sodium hydroxide solution are added, the flask securely closed and digested for at least two hours in a water-bath at 100° . The contents are then washed into a beaker, and titrated with normal acid and phenolphthalein. The difference between the number of cubic centimetres of sodium hydroxide taken and of the acid required for neutralisation may be calculated as methyl acetate, from the equation :—

$$\frac{0.074 \times \text{c.c. of } N/1 \text{ NaOH required} \times 100}{\text{c.c. naphtha taken.}} = \text{g. methyl acetate for 100 c.c.}$$

or, if 5 c.c. of spirit are taken :—

$$1.48 \times \text{c.c. NaOH required} = \text{g. methyl acetate for 100 c.c.}$$

B.—THE ESTIMATION OF METHYL ALCOHOL IN ETHYL ALCOHOL.

T. E. Thorpe and J. Holmes' method¹ depends on the complete oxidation of methyl alcohol to carbon dioxide by means of chromic

¹ *J. Chem. Soc.*, 1904, 85, 1.

acid mixture under certain conditions, ethyl alcohol under the same conditions being oxidised to the extent of only 0.5 per cent. of its weight.

The sample is mixed with water in such proportions that 50 c.c. of the mixture shall contain not more than 4 g. of the mixed alcohols, and not more than 1 g. of methyl alcohol. 50 c.c. of this mixture are then introduced into a 300 c.c. flask, which can be closed by a ground-in stopper, and which is fitted with a side funnel and side tube. 20 g. of potassium bichromate and 80 c.c. of dilute sulphuric acid (1:4) are added, and the mixture allowed to remain for eighteen hours. A further quantity of 10 g. of potassium bichromate and 50 c.c. of sulphuric acid mixed with an equal volume of water are then added, and the contents of the flask heated to the boiling point for about ten minutes, the evolved carbon dioxide being swept out of the apparatus by a current of air and collected in soda lime.

A subtractive correction must be applied to the weight of carbon dioxide thus obtained in the proportion of 0.01 g. carbon dioxide for each 1 g. of ethyl alcohol present.

In this process acetone and methyl acetate are oxidised to acetic acid and carbon dioxide, and allyl alcohol is completely oxidised to carbon dioxide. The bulk of the secondary constituents of wood naphtha used for methylating may be removed from methylated spirit by shaking with light petroleum and saturated salt solution (see p. 721); the saline liquid is then distilled, and the distillate submitted to the oxidation process. It is not possible by this treatment to remove the whole of the constituents other than methyl and ethyl alcohols, and in the case of methylated spirit the methyl alcohol found will usually be about 4 per cent. too high.

If the proportion of methyl alcohol is very small the above method is not well adapted for use, since the necessary subtractive correction may in such cases equal or exceed the quantity it is desired to estimate.

C. Simmonds¹ has shown that in such cases satisfactory determinations can be made by applying the principle of colorimetric comparison to Denigès' method for the detection of methyl alcohol, which depends upon the oxidation of the methyl alcohol to formaldehyde by an acid solution of potassium permanganate.

The alcoholic mixture is first purified, if necessary, by the method given above. It is then diluted with water or mixed with ethyl alcohol as the case may require, until it contains 10 per cent. of total alcohol by volume.

To 5 c.c. of this prepared liquid, contained in a wide test tube, are added 2.5 c.c. of permanganate solution (2.0 g. KMnO_4 per 100 c.c.),

¹ *Analyst*, 1912, 37, 16.

and then 0.2 c.c. of strong sulphuric acid. When the reaction has proceeded for about three minutes, 0.5 c.c. of oxalic acid solution (9.6 g. crystallised acid per 100 c.c.) is added. On shaking, the liquid becomes clear and nearly colourless. 1 c.c. of strong sulphuric acid is then run in and well mixed with the solution, which is finally treated with 5 c.c. of Schiff's reagent. A violet colour is developed in the course of a few minutes unless mere traces of methyl alcohol were present, when twenty to thirty minutes may be required. A sufficient quantity of sulphuric acid is present to prevent the development of colour with any acetaldehyde formed from the ethyl alcohol during the oxidation.

A preliminary experiment carried out as described serves to detect the presence of methyl alcohol, and to give some idea of the quantity present. According to the indications thus obtained, another part of the prepared liquid is further diluted, if necessary, with ethyl alcohol of 10 per cent. strength, until it contains from 0.001-0.004 g. of methyl alcohol in 5 c.c., and the experiment is repeated side by side with two or more standards for comparison. These contain 0.001, 0.002, 0.003, etc., g. of methyl alcohol in 5 c.c. of 10 per cent. ethyl alcohol. The colours produced are compared in small Nessler tubes (25 c.c.) or in a suitable colorimeter.

With properly sensitive Schiff's reagent, 0.0003 g. of methyl alcohol in the 5 c.c. of liquid taken is readily detected. The best depths of colour for comparison, however, are given by the formaldehyde produced in the manner described from quantities of 0.001-0.004 g. of methyl alcohol.

The degree of accuracy obtainable by this process is shown by the following results, given in Simmonds' paper:—

Grams of Methyl Alcohol per 100 c.c.

Present.	Found.
0.005	0.004
0.028	0.029
0.044	0.046
0.072	0.072
0.100	0.104
0.500	0.492
1.000	0.968

A. E. Leach and H. C. Lythgoe¹ recommend the use of the Zeiss immersion refractometer for the analysis of mixtures of methyl and ethyl alcohols. For details of the method and Tables giving the proportions of the two alcohols corresponding to any given refractometer reading, the reader is referred to the original paper.

¹ *J. Amer. Chem. Soc.*, 1905, **27**, 964.

The presence of mineral naphtha in methylated spirit may be detected by diluting the sample with water, when the mineral naphtha separates and causes the liquid to become cloudy.

Methods for the estimation of substances other than methyl alcohol in commercial spirits are described in connection with the secondary constituents of potable spirits (p. 722).

C.—THE ESTIMATION OF ETHYL ALCOHOL IN FUSEL OIL.

Fusel oil containing less than 15 per cent. of proof spirit is admitted duty free into the United Kingdom. The amount of alcohol in fusel oil may be estimated by Thorpe and Holmes' method (p. 721), provided that rather more petroleum spirit and less sodium chloride solution is used. Another method which gives approximately accurate results consists in agitating the sample in a graduated tube with an equal volume of benzene or petroleum spirit, subsequently adding sufficient water to cause the benzene to separate. The increase in the volume of the benzene indicates, with approximate accuracy, the amount of amyl alcohol in the sample under examination (Allen).

VII. POTABLE SPIRITS AND LIQUEURS.

Potable spirits are divided for purposes of excise into two classes:—(1) plain or naturally flavoured spirits, which include Whisky, Brandy, and Rum; and (2) compounded or artificially flavoured spirits, such as Gin, British Brandy, Liqueurs, and Cordials. The flavour and character of plain spirits is dependent on the materials employed and on the methods of distillation and subsequent storage; while compounded spirits are produced either by mixing plain spirits with certain flavouring and sweetening materials, or by redistilling them with herbs, fruits, essences, etc. There is no essential difference between liqueurs and cordials, the name "liqueur" being usually taken to signify a foreign product, and "cordial" a product of British manufacture.

A.—ALCOHOLIC STRENGTH.

According to Section 6 of the Sale of Food and Drugs Act Amendment Act, 1879, the lowest strength at which brandy, whisky, or rum may be sold is 25° under proof, 35° under proof being allowed for gin. The quantity of alcohol present is estimated from the specific gravity of the distillate as given on p. 709. Traces of substances other than ethyl alcohol are usually present in the distillate, and may affect the result to a slight extent, but the error thus introduced is in most cases negligible.

In the case of a neutral or silent spirit the percentage of alcohol may of course be found directly from the specific gravity without previous distillation. Most potable spirits, however, owing to the presence of sweetening or colouring matters in solution, show a higher gravity than would correspond to a simple mixture of alcohol and water of the same strength. "Obscuration" is the term usually applied to indicate the amount of proof spirit thus hidden or "obscured" by matter in solution, or in other words the difference between the true or actual strength and that indicated by the hydrometer. Thus a spirit of 5 over proof by the hydrometer with 3 per cent. obscuration is of an actual strength of 8 over proof.

The limits laid down in Section 6 of the Sale of Food and Drugs Act, 1879, refer, in the case of obscured spirits, to the actual strength ascertained after distillation.

The alcoholic strength of potable spirits containing only slight amounts of non-volatile matter may be approximately ascertained from the specific gravity of the original spirit and the proportion of non-volatile residue. The percentage of non-volatile solids is multiplied by 0.0055 and the number thus obtained subtracted from the specific gravity of the original sample, the result being the specific gravity of a mixture of alcohol and water of the same strength as the sample.

In dealing with spirituous liquids containing considerable amounts of volatile aromatic and essential oils, these must be separated by saturating the liquid with common salt before distilling off the alcohol. For this purpose 100 c.c. of the sample are diluted with water and shaken up with granulated salt in a graduated cylinder of about 300 c.c. capacity; when no more salt will dissolve, the cylinder is allowed to remain at rest until the oils have separated out on the surface as a well-defined layer. A measured portion of the aqueous liquid is then withdrawn and distilled in the ordinary manner. The separated essential oils may be dissolved in ether and further examined if desired.

T. E. Thorpe and J. Holmes¹ give the following method of estimating alcohol in presence of volatile essential oils:—25 c.c. of the sample, measured at 15°.5, are mixed with water in a separating funnel to a bulk of from 100-150 c.c., and sodium chloride added in quantity sufficient to saturate the liquid. The mixture is then shaken vigorously for five minutes with from 50-80 c.c. of light petroleum, boiling below 60°, and after standing for about half an hour, the lower layer is drawn off into another separating funnel, extracted a second time with light petroleum, and then drawn off into a distillation flask. Meanwhile the layers of light petroleum are washed successively with

¹ *J. Chem. Soc.*, 1903, 83, 314.

25 c.c. of saturated sodium chloride solution, and the washings added to the main bulk, which is neutralised if necessary, and then distilled and the distillate made up to 100 c.c.

Many alcoholic liquids show a tendency to froth up on boiling; this may in many cases be overcome by the addition of tannin. Bumping in the flask is best prevented by a few pieces of ignited unglazed earthenware (broken porous tiles); if this is ineffective, steam distillation must be resorted to. If considerable amounts of volatile acids are present, the sample should be neutralised before distilling off the alcohol.

B.—SECONDARY CONSTITUENTS.

The secondary constituents of potable spirits such as brandy, whisky, and rum, to which the flavour and aroma are due, consist mainly of higher alcohols, esters, acids, aldehydes, and furfural. The possibility of distinguishing between spirits derived from grain or molasses and those derived from grape juice by the determination of the secondary constituents has in recent years been largely discounted, and it is admitted to be impossible, except in comparatively few instances, to judge of the genuineness or otherwise of a sample of spirits by any other means than taste and smell. Analysis may often be of value in confirming a palate judgment, and it is found that uniformity in quality, as judged by the palate in the case of any particular brand of spirits, is generally accompanied by remarkable uniformity in the results of analysis. The converse of this is by no means true, and it is possible to prepare two samples of spirits showing approximately the same figures for secondary constituents, but nevertheless of entirely different character.

Although a large number of the secondary constituents of brandy, whisky, and rum have been identified, the quantity of any particular constituent is rarely determined in the course of an ordinary analysis. Unless the analyst has a large amount of material and time at his disposal, all that he can do is to group together in his analysis the total quantities of higher alcohols, esters, etc., in the sample, expressing his results in terms of one member of the group. Thus, higher alcohols are expressed in terms of amyl or isobutyl alcohols, esters in terms of ethyl acetate, and volatile acids as acetic acid, although the different members of these groups may vary considerably in constitution and molecular weight.

According to Ordonneau¹ and others,² the proportion of the higher alcohols present may vary within the following wide limits, according

¹ *Comptes rend.*, 1886, 102, 217.

² Claudon and Morin, *Bull. Soc. Chim.*, 1888, 49, 178; Windisch, *Kaiserlich. gesundheitsamt*, 1893, 8, 214, 288; Behrend, *Z. Spiritusind.*, 1890, 13, 273.

as the spirit is distilled from some kind of grain, potatoes, wine, grape skins, etc.

Alcohol.	Percentage proportion.
Primary propyl alcohol	0.1 to 6.8
Primary butyl alcohol	0 „ 63.8
Isopropyl butyl alcohol	0.4 „ 24.3
Isopropyl amyl alcohol (two)	68.8 „ 99.5
Hexyl alcohol	trace
Heptyl alcohol	„
Glycerol	„
Isobutylene glycol	„

In the case of spirit obtained from the same source, variations are produced by different yeasts or bacteria originally present or accidentally introduced.

1. Total Acidity.

To determine the total acidity 50 c.c. of the sample are titrated with $N/10$ sodium hydroxide or barium hydroxide, using phenolphthalein as indicator.

2. Volatile Acidity.

Another portion of 50 c.c. is evaporated in a beaker to near dryness over a steam-bath, about 25 c.c. of distilled water added, and the solution again evaporated. The residue is then dissolved in about 25 c.c. of cold, recently boiled, distilled water, and titrated with $N/10$ sodium hydroxide or with barium hydroxide as before. The difference between the value so ascertained and that obtained in the previous experiment is a measure of the volatile acidity. The volatile acidity is usually expressed in terms of acetic acid, and the fixed acidity, *i.e.*, the difference between the total and the volatile acidity, in terms of tartaric acid. The results may be expressed either as grams per 100 c.c. of the sample, or as parts per 100,000 of absolute alcohol.

3. Total Solids and Ash.

For this estimation 100 c.c. of the sample, or the residue left in the distilling flask from the distillation test mentioned below, are evaporated to dryness in a tared capsule, dried in a steam-oven at 100° and weighed after cooling in a desiccator. The residue is then ignited at a dull red heat, and when only a white ash remains the capsule is allowed to cool and is weighed. The solids and ash thus determined are expressed in grams per 100 c.c. of the sample. The ash is examined for the presence of lead, copper, iron, etc., and, if necessary, the amount of such substances present estimated by suitable means.

Examination of the Distillate.

Commercial spirits are often slightly sweetened and coloured, usually with caramel. Sometimes the colouring used contains a coal-tar dye. The presence of an artificial dye of this kind can generally be determined by dyeing a fragment of white Berlin wool, and the sugar present may be estimated in the usual way with Fehling's solution. Most commercial spirits, and especially potable spirits such as whisky, brandy, rum, etc., contain various colouring and other matters extracted from the casks in which they have been stored. Before the tests described below can be applied it is necessary, therefore, to free the spirit by redistillation from all extraneous colouring or extractive matter added to it, or derived from the cask. This practice is also advisable even when the spirit appears to be colourless.

The density and apparent strength of the sample as it stands having been ascertained, a measured quantity (120-150 c.c. or more according to strength) is placed in a glass flask, and diluted to nearly 200 c.c. with distilled water. The flask is connected by good rubber stoppers and a bent glass tube with a spiral condenser, and the contents gently distilled to as near dryness as possible without charring the residue. The distillate is made up to 200 c.c., and the strength ascertained as before. The quantity taken for distillation should be such that the distillate will contain about 50 per cent. of absolute alcohol (87.5 per cent. of proof spirit).

4. Acidity of the Distillate.

50 c.c. are titrated with $N/10$ sodium hydroxide solution, using phenolphthalein as indicator. The acid is calculated as acetic acid. The estimation of the acidity is a necessary preliminary to the estimation of the esters. The acidity of the distillate is usually slightly less than the total volatile acid as determined in the sample before distillation.

5. Esters.

A further 10 c.c. of $N/10$ sodium hydroxide solution are added to the neutralised distillate, and the liquid boiled under a reflux condenser for half an hour. A Jena flask should be used in this operation in order to minimise the error caused by the action of the alkali on the glass. In any case a blank experiment should be carried out at the same time on a similar quantity of diluted neutral spirit (*cf.* the determination of the saponification value of fats and oils, this Vol., p. 114). After cooling, the contents of both flasks are titrated with $N/10$ sulphuric or hydrochloric acid and phenolphthalein, and the difference between the two titrations calculated in terms of ethyl acetate.

6. Furfural.

A standard solution is made up containing 1 g. of furfural in 100 c.c. of pure spirit of 50 per cent. strength, and from this other standard solutions are prepared containing 0.1, 0.01, and 0.001 g. respectively of furfural per 100 c.c. in similar spirit.

For the estimation of the furfural 10 c.c. of the distillate to be examined are placed in a Nessler tube, and similar tubes are prepared containing from 0.5 c.c. to 10.0 c.c. of the standard 0.001 per cent. furfural solution, the volumes in each case being made up to 10 c.c. with pure 50 per cent. alcohol. To each tube is added 0.5 c.c. of freshly prepared aniline acetate (made by mixing equal volumes of pure redistilled aniline and acetic acid), and the contents well shaken. When furfural is present a fine pink colour is developed on standing, and at the end of ten to fifteen minutes the sample is compared with the standards. It is not desirable to have a greater depth of colour than that given by 10 c.c. of the standard 0.001 per cent. solution. A sample giving a deeper colour should be diluted with pure 50 per cent. alcohol.

7. Aldehydes.

For the estimation of aldehydes a standard solution is prepared with pure aldehyde-free 50 per cent. alcohol. The aldehyde is best obtained from recrystallised aldehyde-ammonia which has been treated with dehydrated ether and dried over concentrated sulphuric acid, as recommended by Girard and Cuniasse.

A solution containing 1 g. of acetaldehyde in 100 c.c. is prepared with aldehyde-free 50 per cent. alcohol, and from this standard solutions containing 0.1 and 0.01 g. respectively of aldehyde per 100 c.c. are prepared with pure 50 per cent. spirit. 10 c.c. of the distillate under examination are placed in a Nessler tube, and in similar tubes 10 c.c. each of solutions of pure 50 per cent. alcohol containing from 0.5-10 c.c. of the 0.01 per cent. standard aldehyde solution. To each tube is added 1 c.c. of Schiff's reagent, prepared by decolorising a standard fuchsine solution with sodium hydrogen sulphite and sulphuric acid.¹

After shaking, the tubes are allowed to stand for about thirty minutes, when the violet colours developed are compared. If the colour in the sample is greater than that of a 10 c.c. standard (*i.e.* if the distillate shows more than 10 mg. of aldehyde per 100 c.c.), the sample should be diluted with pure aldehyde-free 50 per cent. alcohol.

¹ The usual formula for the reagent is:—0.15 g. fuchsine in 150 c.c. of water, 100 c.c. of sodium hydrogen sulphite solution (sp. gr. 1.36), and 10 c.c. of concentrated sulphuric acid.

8. Higher Alcohols.

Three methods are in common use for the estimation of higher alcohols—the Allen-Marquardt method, used in Great Britain; the Röse-Herzfeld method, which has received official sanction in Germany; and the colorimetric method with sulphuric acid, as used in France. To these may perhaps be added the Beckmann nitrite process, which is, however, but rarely used.

The Allen-Marquardt Method is the only one which may be said to rest upon a sound scientific basis, inasmuch as it depends upon the complete oxidation of the higher alcohols to their corresponding acids, and the estimation of these by titration with a standard solution of barium hydroxide. The barium salts of the acids may subsequently be recovered, and the mean combining weight of the acids deduced therefrom as a check upon the analysis.

In this method 200 c.c. of the sample are boiled for an hour under a reflux condenser with 1 c.c. of strong potassium hydroxide solution. The liquid is then distilled until only about 20 c.c. remain in the flask, and the distillation continued from this point with steam until 300 c.c. of distillate in all have been collected, and the residue in the flask measures about 10 c.c. The distillate is divided into two parts for further treatment, thus giving a duplicate determination of the higher alcohols.

The liquid is brought to a specific gravity of at least 1.1 by the addition of a saturated solution of common salt, and extracted in a separating funnel four times with carbon tetrachloride, using 40, 30, 20, and 10 c.c. respectively of the solvent for the four extractions. Inasmuch as a certain amount of ethyl alcohol is extracted by the carbon tetrachloride together with the higher alcohols, this must be removed by shaking up with 50 c.c. of brine. After being shaken with 50 c.c. of saturated sodium sulphate solution to remove chlorides, the liquid is ready for the oxidation of the higher alcohols to their corresponding acids by means of chromic acid. For this purpose it is treated with 5 g. of potassium bichromate, 2 g. of concentrated sulphuric acid, and 10 c.c. of water, and kept gently boiling on a water-bath for at least eight hours in a flask attached to a reflux condenser. E. A. Mann and T. N. Kirton¹ recommend that the oxidation be carried out in pressure bottles at 98° for four hours, as being quicker and more convenient than heating under a reflux condenser. The liquid, after oxidation, is diluted with 30 c.c. of water, and submitted to distillation over a free flame until about 20 c.c. remain in the flask. Steam is then led in exactly as in the first distillation until about 5-10 c.c. remain and the combined distillate measures 300 c.c.

¹ *J. Soc. Chem. Ind.*, 1907, 26, 450.

The distillate is then carefully rendered neutral to methyl orange with $N/10$ barium hydroxide solution, with repeated shaking. As a rule, not more than 2 c.c. of this solution will be required. Phenolphthalein is added, and the titration continued until the neutral point is reached with this indicator. Each cubic centimetre of $N/10$ barium hydroxide required in the second stage of the titration corresponds to 0.0088 g. of amyl alcohol.

P. Schidrowitz and F. Kaye¹ have subjected the Allen-Marquardt method to a critical examination, and find that, although traces of ethyl alcohol may remain in the carbon tetrachloride before oxidation, this yields practically no acetic acid, being mainly converted into some non-acidic substance. They further point out that Allen's original opinion that the "methyl orange acidity" is due to mineral acid, *i.e.*, in this case hydrochloric acid, is not justified. They found that although the amount of mineral acid thus found varied widely in a number of estimations, it always corresponded roughly to one-tenth of the whole titration. When the chlorine present in the distillate was determined, it was always found to be much less than would correspond to the "mineral acid" as found by methyl orange titration. They suggest that this anomaly is due to the fact that under certain conditions the lower fatty acids are not absolutely neutral to methyl orange, and recommend that the total acidity be calculated in terms of amyl alcohol. If the methyl orange acidity is greater than 10 per cent. of the whole, the result should be corrected by a separate chlorine estimation.

As mentioned above, a useful check on the analysis is afforded by determining the mean equivalent of the acids from the weight of the barium salts. For this purpose the distillate after titration is evaporated to dryness, and the residue dried at 130° and weighed. The weight of barium in the residue being known from the results of titration, the mean combining weight of the acids can be calculated in the usual manner.

The carbon tetrachloride used should be first shaken with water, then boiled for several hours with the chromic acid mixture, subsequently washed with water, then with very dilute sodium bicarbonate solution, and finally again with distilled water until neutral; or, after treatment with the chromic acid mixture, it may be purified by distilling over barium carbonate.

The corks used in the distillation of the spirit must be kept separate from those used during and after the oxidation process. They should be covered with tin-foil to prevent the absorption of amyl alcohol and of valeric acid; ground glass joints, if available, are better than corks. The condenser tube used during the chromic acid oxidation should be as efficient as possible.

¹ *Analyst*, 1905, 30, 190; 1906, 31, 181.

The Röse-Herzfeld Method of estimating higher alcohols (fusel oil) depends upon the increase in volume of chloroform when shaken up with the spirit under certain strictly defined conditions. The method has been examined and criticised by V. H. Veley¹ and by P. Schidrowitz,² and it is probable that if scrupulous care be taken to observe minutely the somewhat tedious precautions necessary, the method may be regarded as accurate for commercial purposes in cases where a comparatively large amount of fusel oil is present. In view of the fact that an estimation of higher alcohols either by the Röse-Herzfeld or by the colorimetric method may occasionally be necessary for purposes of comparison with the results obtained by continental chemists, a detailed description of them is given here.

Röse originally recommended that the distillate from the sample should be brought to exactly 50 per cent. by volume before extraction with chloroform. But inasmuch as in the majority of cases this necessitated the addition of pure alcohol to the distillate, Stutzer and Reitmaier proposed the substitution of 30 per cent. by volume as the strength to which the distillate should be brought. The method as adopted in the German Public Health Department is based on a long series of careful observations on the behaviour of chloroform when shaken up with pure 30 per cent. alcohol, and with the same alcohol containing varying amounts of fusel oil.

The apparatus ("fusel-oil tube") used, as modified by Herzfeld, consists of a 20 c.c. bulb surmounted by a graduated tube opening into a much larger bulb (150-180 c.c.). The graduation on the tube is so adjusted that when filled to the lowest mark the vessel contains exactly 20 c.c. The tube itself holds about 6 c.c., and is graduated in divisions of $\frac{1}{20}$ c.c. These divisions are at least 1.4 mm. apart, so that it is possible to read approximately to 0.01 c.c. The larger of the two bulbs is closed by a glass stopper. The vessel should be carefully cleaned before use with hot sulphuric acid, and dried with alcohol and ether, care being taken to remove the last traces of ether. The sample of spirits must be distilled with caustic alkali before being submitted to the test.

To carry out the estimation a few drops of strong sodium hydroxide solution are added to 100 c.c. of the sample, 80 c.c. distilled over, and the distillate made up to 100 c.c. Distillation with alkali is absolutely necessary in all cases, and it is advisable to boil the liquid before distilling under a reflux condenser for one hour with the sodium hydroxide, in order to remove carbon dioxide, aldehydes, and esters, which may affect the accuracy of the method to a considerable extent.

The specific gravity of the distillate is then determined with the

¹ *J. Soc. Chem. Ind.*, 1906, 25, 398.

² *Ibid.*, 1902, 21, 814.

greatest care by the pyknometer, and the content of alcohol ascertained by reference to the Table on p. 711.

The distillate must then be diluted so as to contain exactly 24.7 per cent. of alcohol by weight (30 per cent. by volume). The accompanying Tables 58 and 59 give the quantity of water or alcohol which must be added to distillates of various strengths in order to bring them exactly to 24.7 per cent. of alcohol by weight. Both the distillate and the alcohol or water to be added must be at 15°. The strength must then be checked by a second determination of the specific gravity by the pyknometer. Two "fusel oil tubes" are supported in a large vessel of water at 15°, and 20 c.c. of pure chloroform are introduced into each through a funnel tube in such a way that the walls of the graduated tube are not wetted, and that the chloroform reaches exactly to the lowest graduation mark. Any excess of chloroform is removed by means of a capillary glass tube. Into each tube are introduced 100 c.c. of the distillate previously adjusted as above to exactly 30 per cent. by volume of alcohol, and brought to a temperature of 15°; 1 c.c. of dilute sulphuric acid (sp. gr. 1.286) is then added. The tubes are closed with the stoppers, and allowed to remain a quarter of an hour in the bath at 15°. They are then taken out alternately, inverted so that the whole of the contents are transferred into the larger bulb, and shaken vigorously about 150 times, after which they are replaced in the water-bath for an hour. The chloroform sinks rapidly to the bottom, and by gently rotating and tapping the tubes a sharp line of separation between the liquids is obtained. It is very important that the temperature of the water-

Table 58.

Table for Distillates containing less than 24.7 per cent. of Alcohol by Weight.

Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.
22.50	3.52	23.05	2.63	23.60	1.74	24.15	0.85
22.55	3.44	23.10	2.55	23.65	1.66	24.20	0.77
22.60	3.36	23.15	2.47	23.70	1.58	24.25	0.69
22.65	3.28	23.20	2.39	23.75	1.50	24.30	0.61
22.70	3.20	23.25	2.31	23.80	1.42	24.35	0.53
22.75	3.11	23.30	2.23	23.85	1.34	24.40	0.45
22.80	3.04	23.35	2.15	23.90	1.26	24.45	0.37
22.85	2.96	23.40	2.07	23.95	1.18	24.50	0.29
22.90	2.88	23.45	1.98	24.00	1.09	24.55	0.21
22.95	2.79	23.50	1.90	24.05	1.01	24.60	0.12
23.00	2.71	23.55	1.82	24.10	0.93	24.65	0.04

Table 59.

Table for Distillates containing more than 24.7 per cent. of Alcohol by Weight.

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
24.7	0.1	29.9	20.3	35.1	40.1	40.3	59.5	45.5	78.3	50.7	96.7		
24.8	0.5	30.0	20.7	35.2	40.5	40.4	59.8	45.6	78.7	50.8	97.1		
24.9	0.9	30.1	21.0	35.3	40.8	40.5	60.2	45.7	79.1	50.9	97.4		
25.0	1.3	30.2	21.4	35.4	41.2	40.6	60.6	45.8	79.4	51.0	97.8		
25.1	1.7	30.3	21.8	35.5	41.6	40.7	60.9	45.9	79.8	51.1	98.1		
25.2	2.0	30.4	22.2	35.6	42.0	40.8	61.3	46.0	80.1	51.2	98.5		
25.3	2.4	30.5	22.6	35.7	42.3	40.9	61.7	46.1	80.5	51.3	98.8		
25.4	2.8	30.6	23.0	35.8	42.7	41.0	62.0	46.2	80.8	51.4	99.1		
25.5	3.2	30.7	23.3	35.9	43.1	41.1	62.4	46.3	81.2	51.5	99.5		
25.6	3.6	30.8	23.7	36.0	43.5	41.2	62.8	46.4	81.6	51.6	99.8		
25.7	4.0	30.9	24.1	36.1	43.8	41.3	63.1	46.5	81.9	51.7	100.2		
25.8	4.4	31.0	24.5	36.2	44.2	41.4	63.5	46.6	82.3	51.8	100.5		
25.9	4.8	31.1	24.9	36.3	44.6	41.5	63.9	46.7	82.6	51.9	100.9		
26.0	5.2	31.2	25.3	36.4	45.0	41.6	64.2	46.8	83.0	52.0	101.2		
26.1	5.6	31.3	25.6	36.5	45.3	41.7	64.6	46.9	83.3	52.1	101.6		
26.2	5.9	31.4	26.0	36.6	45.7	41.8	65.0	47.0	83.7	52.2	101.9		
26.3	6.3	31.5	26.4	36.7	46.1	41.9	65.3	47.1	84.1	52.3	102.3		
26.4	6.7	31.6	26.8	36.8	46.5	42.0	65.7	47.2	84.4	52.4	102.6		
26.5	7.1	31.7	27.2	36.9	46.8	42.1	66.1	47.3	84.8	52.5	102.9		
26.6	7.5	31.8	27.6	37.0	47.2	42.2	66.4	47.4	85.1	52.6	103.3		
26.7	7.9	31.9	27.9	37.1	47.6	42.3	66.8	47.5	85.5	52.7	103.6		
26.8	8.3	32.0	28.3	37.2	48.0	42.4	67.1	47.6	85.8	52.8	104.0		
26.9	8.7	32.1	28.7	37.3	48.3	42.5	67.5	47.7	86.2	52.9	104.3		
27.0	9.1	32.2	29.1	37.4	48.7	42.6	67.9	47.8	86.5	53.0	104.7		
27.1	9.4	32.3	29.5	37.5	49.1	42.7	68.2	47.9	86.9	53.1	105.0		
27.2	9.8	32.4	29.8	37.6	49.5	42.8	68.6	48.0	87.2	53.2	105.3		
27.3	10.2	32.5	30.2	37.7	49.8	42.9	69.0	48.1	87.6	53.3	105.7		
27.4	10.6	32.6	30.6	37.8	50.2	43.0	69.3	48.2	87.9	53.4	106.0		
27.5	11.0	32.7	31.0	37.9	50.6	43.1	69.7	48.3	88.3	53.5	106.4		
27.6	11.4	32.8	31.4	38.0	51.0	43.2	70.0	48.4	88.7	53.6	106.7		
27.7	11.8	32.9	31.7	38.1	51.4	43.3	70.4	48.5	89.0	53.7	107.1		
27.8	12.2	33.0	32.1	38.2	51.7	43.4	70.8	48.6	89.4	53.8	107.4		
27.9	12.6	33.1	32.5	38.3	52.1	43.5	71.1	48.7	89.7	53.9	107.7		
28.0	12.9	33.2	32.9	38.4	52.4	43.6	71.5	48.8	90.1	54.0	108.1		
28.1	13.3	33.3	33.3	38.5	52.8	43.7	71.9	48.9	90.4	54.1	108.4		
28.2	13.7	33.4	33.7	38.6	53.2	43.8	72.3	49.0	90.8	54.2	108.8		
28.3	14.1	33.5	34.0	38.7	53.5	43.9	72.6	49.1	91.1	54.3	109.1		
28.4	14.5	33.6	34.4	38.8	53.9	44.0	72.9	49.2	91.5	54.4	109.5		
28.5	14.9	33.7	34.8	38.9	54.3	44.1	73.3	49.3	91.8	54.5	109.8		
28.6	15.3	33.8	35.2	39.0	54.7	44.2	73.7	49.4	92.2	54.6	110.1		
28.7	15.6	33.9	35.5	39.1	55.0	44.3	74.0	49.5	92.5	54.7	110.5		
28.8	16.0	34.0	35.9	39.2	55.4	44.4	74.4	49.6	92.9	54.8	110.8		
28.9	16.4	34.1	36.3	39.3	55.7	44.5	74.7	49.7	93.2	54.9	111.2		
29.0	16.8	34.2	36.7	39.4	56.1	44.6	75.1	49.8	93.6	55.0	111.5		
29.1	17.2	34.3	37.1	39.5	56.5	44.7	75.5	49.9	93.9	55.1	111.8		
29.2	17.6	34.4	37.4	39.6	56.9	44.8	75.8	50.0	94.3	55.2	112.2		
29.3	18.0	34.5	37.8	39.7	57.2	44.9	76.2	50.1	94.6	55.3	112.5		
29.4	18.3	34.6	38.2	39.8	57.6	45.0	76.5	50.2	95.0	55.4	112.9		
29.5	18.7	34.7	38.6	39.9	58.0	45.1	76.9	50.3	95.3	55.5	113.2		
29.6	19.1	34.8	39.0	40.0	58.4	45.2	77.3	50.4	95.7	55.6	113.5		
29.7	19.5	34.9	39.3	40.1	58.7	45.3	77.6	50.5	96.0	55.7	113.9		
29.8	19.9	35.0	39.7	40.2	59.1	45.4	78.0	50.6	96.4	55.8	114.2		

Table 59.
Table for Distillates—continued.

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
55.9	114.6	61.2	132.2	66.5	149.3	71.8	165.8	77.1	181.8	82.4	197.1
56.0	114.9	61.3	132.5	66.6	149.6	71.9	166.1	77.2	182.1	82.5	197.4
56.1	115.2	61.4	132.9	66.7	149.9	72.0	166.4	77.3	182.4	82.6	197.7
56.2	115.6	61.5	133.2	66.8	150.2	72.1	166.7	77.4	182.6	82.7	197.9
56.3	115.9	61.6	133.5	66.9	150.6	72.2	167.0	77.5	182.9	82.8	198.2
56.4	116.2	61.7	133.8	67.0	150.9	72.3	167.4	77.6	183.2	82.9	198.5
56.5	116.6	61.8	134.2	67.1	151.2	72.4	167.7	77.7	183.5	83.0	198.8
56.6	116.9	61.9	134.5	67.2	151.5	72.5	168.0	77.8	183.8	83.1	199.1
56.7	117.3	62.0	134.8	67.3	151.8	72.6	168.3	77.9	184.1	83.2	199.4
56.8	117.6	62.1	135.2	67.4	152.1	72.7	168.6	78.0	184.4	83.3	199.6
56.9	117.9	62.2	135.5	67.5	152.5	72.8	168.9	78.1	184.7	83.4	199.9
57.0	118.3	62.3	135.8	67.6	152.8	72.9	169.2	78.2	185.0	83.5	200.2
57.1	118.6	62.4	136.1	67.7	153.1	73.0	169.5	78.3	185.3	83.6	200.5
57.2	118.9	62.5	136.5	67.8	153.4	73.1	169.8	78.4	185.6	83.7	200.8
57.3	119.3	62.6	136.8	67.9	153.7	73.2	170.1	78.5	185.9	83.8	201.0
57.4	119.6	62.7	137.1	68.0	154.0	73.3	170.4	78.6	186.2	83.9	201.3
57.5	119.9	62.8	137.4	68.1	154.4	73.4	170.7	78.7	186.5	84.0	201.6
57.6	120.3	62.9	137.8	68.2	154.7	73.5	171.0	78.8	186.7	84.1	201.9
57.7	120.6	63.0	138.1	68.3	155.0	73.6	171.3	78.9	187.0	84.2	202.1
57.8	120.9	63.1	138.4	68.4	155.3	73.7	171.6	79.0	187.3	84.3	202.4
57.9	121.3	63.2	138.7	68.5	155.6	73.8	171.9	79.1	187.6	84.4	202.7
58.0	121.6	63.3	139.0	68.6	155.9	73.9	172.2	79.2	187.9	84.5	203.0
58.1	122.0	63.4	139.4	68.7	156.2	74.0	172.5	79.3	188.2	84.6	203.3
58.2	122.3	63.5	139.7	68.8	156.5	74.1	172.8	79.4	188.5	84.7	203.5
58.3	122.6	63.6	140.0	68.9	156.9	74.2	173.1	79.5	188.8	84.8	203.8
58.4	123.0	63.7	140.3	69.0	157.2	74.3	173.4	79.6	189.1	84.9	204.1
58.5	123.3	63.8	140.7	69.1	157.5	74.4	173.7	79.7	189.4	85.0	204.4
58.6	123.6	63.9	141.0	69.2	157.8	74.5	174.0	79.8	189.6	85.1	204.6
58.7	124.0	64.0	141.3	69.3	158.1	74.6	174.3	79.9	189.9	85.2	204.9
58.8	124.3	64.1	141.6	69.4	158.4	74.7	174.6	80.0	190.2	85.3	205.2
58.9	124.6	64.2	142.0	69.5	158.7	74.8	174.9	80.1	190.5	85.4	205.5
59.0	124.9	64.3	142.3	69.6	159.0	74.9	175.2	80.2	190.8	85.5	205.7
59.1	125.3	64.4	142.6	69.7	159.3	75.0	175.5	80.3	191.1	85.6	206.0
59.2	125.6	64.5	142.9	69.8	159.7	75.1	175.8	80.4	191.4	85.7	206.3
59.3	125.9	64.6	143.2	69.9	160.0	75.2	176.1	80.5	191.7	85.8	206.6
59.4	126.3	64.7	143.6	70.0	160.3	75.3	176.4	80.6	192.0	85.9	206.8
59.5	126.6	64.8	143.9	70.1	160.6	75.4	176.7	80.7	192.2	86.0	207.1
59.6	126.9	64.9	144.2	70.2	160.9	75.5	177.0	80.8	192.5	86.1	207.4
59.7	127.3	65.0	144.5	70.3	161.2	75.6	177.3	80.9	192.8	86.2	207.7
59.8	127.6	65.1	144.8	70.4	161.5	75.7	177.6	81.0	193.1	86.3	207.9
59.9	127.9	65.2	145.2	70.5	161.8	75.8	177.9	81.1	193.4	86.4	208.2
60.0	128.3	65.3	145.5	70.6	162.1	75.9	178.2	81.2	193.7	86.5	208.5
60.1	128.6	65.4	145.8	70.7	162.4	76.0	178.5	81.3	194.0	86.6	208.8
60.2	128.9	65.5	146.1	70.8	162.8	76.1	178.8	81.4	194.3	86.7	209.0
60.3	129.2	65.6	146.4	70.9	163.1	76.2	179.1	81.5	194.5	86.8	209.3
60.4	129.6	65.7	146.8	71.0	163.4	76.3	179.4	81.6	194.8	86.9	209.6
60.5	129.9	65.8	147.1	71.1	163.7	76.4	179.7	81.7	195.1	87.0	209.9
60.6	130.2	65.9	147.4	71.2	164.0	76.5	180.0	81.8	195.4	87.1	210.1
60.7	130.6	66.0	147.7	71.3	164.3	76.6	180.3	81.9	195.7	87.2	210.4
60.8	130.9	66.1	148.0	71.4	164.6	76.7	180.6	82.0	196.0	87.3	210.7
60.9	131.2	66.2	148.3	71.5	164.9	76.8	180.9	82.1	196.2	87.4	210.9
61.0	131.5	66.3	148.7	71.6	165.2	76.9	181.2	82.2	196.5	87.5	211.2
61.1	131.9	66.4	149.0	71.7	165.5	77.0	181.5	82.3	196.8	87.6	211.5

Table 59.

Table for Distillates—*continued*.

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
87.7	211.7	89.8	217.3	91.9	222.8	94.0	228.1	96.1	233.3	98.1	238.1
87.8	212.0	89.9	217.6	92.0	223.1	94.1	228.4	96.2	233.5	98.2	238.3
87.9	212.3	90.0	217.9	92.1	223.3	94.2	228.6	96.3	233.8	98.3	238.5
88.0	212.6	90.1	218.1	92.2	223.6	94.3	228.9	96.4	234.0	98.4	238.8
88.1	212.8	90.2	218.4	92.3	223.8	94.4	229.1	96.5	234.3	98.5	239.0
88.2	213.1	90.3	218.7	92.4	224.1	94.5	229.4	96.6	234.5	98.6	239.2
88.3	213.4	90.4	218.9	92.5	224.3	94.6	229.6	96.7	234.7	98.7	239.5
88.4	213.6	90.5	219.2	92.6	224.6	94.7	229.9	96.8	235.0	98.8	239.7
88.5	213.9	90.6	219.4	92.7	224.9	94.8	230.1	96.9	235.2	98.9	239.9
88.6	214.2	90.7	219.7	92.8	225.1	94.9	230.4	97.0	235.5	99.0	240.1
88.7	214.4	90.8	220.0	92.9	225.4	95.0	230.6	97.1	235.7	99.1	240.4
88.8	214.7	90.9	220.2	93.0	225.6	95.1	230.9	97.2	235.9	99.2	240.6
88.9	215.0	91.0	220.5	93.1	225.9	95.2	231.1	97.3	236.2	99.3	240.8
89.0	215.2	91.1	220.7	93.2	226.1	95.3	231.3	97.4	236.4	99.4	241.1
89.1	215.5	91.2	221.0	93.3	226.4	95.4	231.6	97.5	236.6	99.5	241.3
89.2	215.8	91.3	221.3	93.4	226.6	95.5	231.9	97.6	236.9	99.6	241.5
89.3	216.0	91.4	221.5	93.5	226.9	95.6	232.1	97.7	237.1	99.7	241.8
89.4	216.3	91.5	221.8	93.6	227.1	95.7	232.3	97.8	237.3	99.8	242.0
89.5	216.6	91.6	222.0	93.7	227.4	95.8	232.6	97.9	237.6	99.9	242.2
89.6	216.8	91.7	222.3	93.8	227.6	95.9	232.8	98.0	237.8	100.0	242.4
89.7	217.1	91.8	222.5	93.9	227.9	96.0	233.1				

bath should be kept constant during the whole of the experiment. When a sharp line of separation has been obtained, the height of the chloroform in the graduated tube is read off.

In order to calculate the content of the sample in higher alcohols, the increase of volume undergone by the chloroform when shaken up in the above manner with perfectly pure alcohol of 24.7 per cent. strength (by weight) must first be determined. For this purpose the purest neutral spirit is distilled with sodium hydroxide, and the intermediate fractions of the distillate taken, rejecting the first 20 per cent. and the last 60 per cent. The intermediate fractions should again be distilled, rejecting the first and last runnings. A blank estimation should be carried out three or four times with pure alcohol prepared in this manner on every new tube and every fresh sample of chloroform. The chloroform must be kept away from the light in vessels of brown glass.

The calculation is carried out as follows:—If the volume of the chloroform in the blank experiment on pure alcohol is b cubic centimetres, and in the case of the sample under examination a cubic centimetres, then $(a-b) \times 2.22$ is the percentage of higher alcohols in the sample.

One great disadvantage in this method is the smallness of the $a-b$ reading as compared with a and b . A possible error of 0.01 c.c. in the reading may mean an error of over 20 parts of higher alcohols per 100,000 parts of absolute alcohol.

Although this method is of undoubted value for samples of spirits containing large quantities of fusel oil, it is doubtful whether it is applicable to ordinary "plain spirits." Reference may be made to a paper by W. L. Dudley¹ for additional details of the precautions to be observed in carrying out the process.

The Sulphuric Acid (Colorimetric) Method appears to be used almost exclusively by French chemists. It depends upon the coloration produced by heating alcohol containing higher alcohols with concentrated sulphuric acid. The coloration is compared with that produced by a standard solution of isobutyl alcohol treated with sulphuric acid in exactly the same manner. Aldehydes are first removed by heating the sample under a reflux condenser with metaphenylene diamine or with calcium phenylhydrazine sulphonate (Hewitt's reagent), and subsequently distilling. Veley² has shown that if the isobutyl alcohol and the sulphuric acid are perfectly pure, there is practically no coloration produced on heating, so that the whole basis upon which the method rests would seem to be destroyed. It has been proposed to use amyl alcohol in place of isobutyl as a standard, but this procedure appears to be open to the same objection. Thorpe³ refers to the use of a mixture containing propyl alcohol (1 part), isobutyl alcohol (2 parts), amyl alcohol (3 parts), and capryl alcohol (1 part), as a standard to which the estimations are referred, it being claimed that this mixture is some approximation to the average composition of the "fusel oil" alcohols of pot-still spirits.

The method, as carried out in France, is as follows:—50 c.c. of the sample, adjusted to contain 50 per cent. of absolute alcohol, are placed in a flask of about 250 c.c. capacity, and 1 g. of metaphenylene diamine added, together with a little pumice. The flask is attached to a reflux condenser, and the contents boiled gently for an hour and then allowed to cool. The contents of the flask are then distilled to near dryness and the distillate made up to the original volume of 50 c.c. with a few drops of distilled water. 10 c.c. of the spirit thus prepared are placed in a thoroughly clean flask of about 75 c.c. capacity and 10 c.c. of pure concentrated sulphuric acid are carefully run into the flask so that it forms a layer under the spirit. The contents of the flask are quickly mixed and heated over a naked Bunsen flame, with constant agitation, for fifteen seconds after the commencement of ebullition. It is then set aside to cool, the mouth of the flask being covered with a small

¹ *J. Amer. Chem. Soc.*, 1908, **30**, 1271.

² *Loc. cit.*

³ *Report of Royal Commission on Whisky and other Potable Spirits*, 1908-9, part ii., Appendix Q.

watch-glass. One or more samples of pure alcohol of 50 per cent. strength, and containing known quantities of isobutyl alcohol (0.05 g. or less per 100 c.c.), are treated in exactly the same way. When cold, the coloration given by the sample under examination is compared with that given by the standard samples.

In **Beckmann's Nitrite Method** the higher alcohols are extracted with carbon tetrachloride and converted into their nitrites, the nitrites being subsequently decomposed and the nitrous acid estimated by permanganate. This process is not often used. A set of comparative estimations by the Allen-Marquardt, the Beckmann, and the Sulphuric Acid (colorimetric) methods is given in the *Report of the Royal Commission on Whisky, etc.*, 1908-9, part ii., Appendix Q, and part i., Appendices E and F.¹

The French chemists lay stress on the *Coefficient of Impurities* which is the sum total of the acids, aldehydes, esters, furfural, and higher alcohols expressed in parts per 100,000 of absolute alcohol. For Cognac pot-still brandy it is claimed that this figure never falls below 300, the minimum figure for esters being 100 parts, and for higher alcohols 120 parts per 100,000 of absolute alcohol. There is little doubt that for genuine Cognac brandies distilled in the usual manner in simple pot stills these figures are approximately correct. The Royal Commission of 1909, however, came to the conclusion that the term "brandy," while applicable to a potable spirit manufactured from fermented grape juice and from no other materials, cannot be controlled by the nature of the apparatus or process used in the distillation of the spirit. In the same way whisky was defined as a spirit obtained by distillation from a mash of cereal grains saccharified by the diastase of malt.

The large number of analyses of brandies of different origin and of pot- and patent-still whiskies contained in the Appendices to the Report of the 1909 Commission, indicate the wide variations in composition that may occur through slight differences in the method of preparation or through differences in age, method of storage, etc. Reference to these tables of analyses will show how impossible it is in the majority of cases to express an opinion on any sample of spirits from the results of analysis alone.

In addition to the secondary constituents natural to distilled spirits, they may also contain sweetening or colouring materials, and are sometimes treated with "mellowing" agents with the object of imparting to them the soft flavour of old spirits. Several such mellowing agents have been patented, and most of them have a sugar or fruit basis. The colouring of whisky is usually effected by storage in sherry casks, but frequently caramel is added in small quantities. Caramel is usually present in Cognac brandies where uniformity of colour is required in a

¹ Cf. also papers by P. Schidrowitz and F. Kaye, *Analyst*, 1905, 30, 190; 1906, 31, 181.

particular brand. Aniline dyes are not often met with except in liqueurs. If their presence is suspected, they may be detected by the methods referred to on p. 740.

POTABLE SPIRITS.

1. Whisky.

Whisky is distilled from a fermented mash of malt alone or of malt and grain of various kinds. In general it may be said that Scotch pot-still whisky is distilled from barley malt alone, and Irish pot-still whisky from a mixed mash of malted or unmalted barley with a small proportion of wheat, oats, and rye. This is by no means, however, always the case, and some Irish pot-still distilleries use malt only, while in Scotland a mixed mash is occasionally used. Maize is extensively used in the production of patent-still whisky in both Scotland and Ireland. The whisky sold to the consumer in England is practically always a blend of pot- and patent-still spirit.

2. Brandy.

The brandy consumed in England is mainly imported from France, although increasing quantities are now obtained from Algeria, Spain, Egypt, California, Australia, etc.

Cognac Brandy is essentially a pot-still product and is produced in a comparatively small area in the Charente. The cheaper qualities are frequently blends of pot-still brandy with patent-still spirit produced from grapes in the Midi districts of France. A certain amount of spirit imported to this country consists of grape brandy mixed with rectified beet or grain spirit. *British Brandy* is a compounded spirit prepared by a rectifier or compounder by redistilling duty-paid spirits, made from grain, with flavouring ingredients, or by adding flavouring materials to such spirits.

Hamburg Brandy is stated to be manufactured in Germany from potato or beet spirit, and flavoured so as to imitate grape brandy.

The non-volatile constituents of Cognac brandy may consist of a small proportion of cane sugar, caramel (added for colouring purposes), and tannin and other extractives derived from the casks in which it is stored.

3. Rum.

Rum was defined in the Report of the 1909 Commission as a spirit distilled direct from sugar-cane products in sugar-cane growing countries. Genuine rums belong to two distinct types, Jamaica rum being representative of the first, and Demerara rum of the second. The first type is the result of slow fermentation, lasting from ten to twelve

days, of wash set at a relatively high density (1.072-1.092); the second is the result of a rapid fermentation, lasting from thirty-six to forty-eight hours, of wash set at a low density, usually about 1.060.

Rum is characterised by its high content of volatile acids and esters and by the presence of formic esters and free formic acid. Formic acid may be detected by evaporating the sample nearly to dryness with a slight excess of sodium hydroxide and distilling the residue with phosphoric acid. The distillate reduces ammoniacal silver nitrate solution if formic acid be present, and gives the other reactions of formic acid. Rum also contains a large proportion of ethyl butyrate.

Imitation Rum is largely imported from Germany, being made from patent-still grain or beet spirit flavoured with artificial essences. A certain amount of rum with a very high content of esters (2000-3000 parts for 100,000 of absolute alcohol) is made in Jamaica by what is termed the "high ether process" and exported to Germany for blending with patent-still spirits for the production of "Imitation Rum."

4. Gin.

Gin is prepared from neutral grain spirit either by redistilling it from juniper berries or by treating it with oil of juniper, turpentine, or other flavouring materials. It is usually very free from fusel oil, free acid, tannin, etc. It may be either sweetened or unsweetened.

Geneva or *Hollands* is a spirit with a distinctive flavour, which differs somewhat from English gin. It is prepared from a mixed mash of malted barley, rye, and maize in equal proportions, the wash being distilled three times in a pot still and then redistilled with juniper berries and other flavourings.

5. Kirschwasser.

Kirschwasser is a spirit obtained by the distillation of the fermented juice of the wild cherry in certain parts of Germany. Genuine Kirsch always contains a small proportion of hydrocyanic acid, usually from 0.03-0.05 g. per litre. Only traces of benzaldehyde are present.

Imitation Kirsch prepared from grain spirit flavoured with peach stones, cherry laurel leaves, etc., may contain up to 0.20 g. of hydrocyanic acid per litre. Grain spirit flavoured with oil of bitter almonds and sweetened is sometimes sold as kirschwasser. Such preparations contain only traces of hydrocyanic acid (up to 0.005 g. per litre) together with comparatively large amounts of benzaldehyde. Hydrocyanic acid may be detected in the distillate from a sample of kirschwasser by the ferrocyanide test as given by G. D. Lander and A. E. Walden.¹ A small portion of the distillate is treated with 2 drops of a

¹ *Analyst*, 1911, 36, 266.

10 per cent. sodium hydroxide solution and evaporated nearly to dryness. To the cooled residue is added 1 drop of 2 per cent. ferrous sulphate solution and the mixture allowed to stand for fifteen minutes; 2-3 drops of strong hydrochloric acid are then added, and the solution warmed gently and cooled. On careful dilution of the liquid, a blue colour will be obtained if hydrocyanic acid was present. E. Berl and M. Delpy¹ have shown that excellent quantitative results may be obtained by the ferrocyanide method. Full details of the method are given in their paper and in that of Lander and Walden.

The Estimation of Hydrocyanic Acid and of Benzaldehyde.—

For the estimation of these substances 100-200 c.c. of the sample are treated with 10-15 drops of concentrated potassium hydroxide solution and distilled until about 20 c.c. remain. To the distillate are added 3 or 4 c.c. of a solution containing phenylhydrazine hydrochloride (2 parts), crystallised sodium acetate (3 parts), and distilled water (20 parts). The liquid is then diluted with sufficient distilled water to reduce the alcoholic strength to about 25 per cent. by volume, well shaken, and allowed to stand for at least two hours. It is then filtered and the precipitate washed with dilute (25 per cent.) alcohol. The precipitate is dissolved off the filter with a small quantity of absolute alcohol, and the solution evaporated in a tared flask at 80° or under reduced pressure. The weight of the precipitate multiplied by 0.540 gives the amount of benzaldehyde contained in the original liquid.

The residue remaining in the flask is diluted with water, slightly acidified with phosphoric acid, and distilled, when the whole of the hydrocyanic acid passes over in the first five or ten minutes. The distillate is treated with 2 drops of concentrated hydrochloric acid, and titrated with $N/100$ silver nitrate solution. The end of the titration is indicated by the appearance of a slight opalescence due to the formation of silver chloride. Each cubic centimetre of $N/100$ silver nitrate solution corresponds to 0.0108 g. of HCN per 100 c.c. of the original sample.

LIQUEURS, BITTERS, AND CORDIALS.

The basis of most liqueurs is neutral or silent spirit distilled from grain or grape juice. The spirit is flavoured by the addition of essential oils, vegetable extracts, and bitters, and is sweetened either with cane sugar or invert sugar. Some liqueurs, such as *Chartreuse*, *Curaçao*, and *Anisette*, are distilled from a complex mixture of herbs and the distillate subsequently sweetened and coloured; others, such as *Cherry Brandy* and *Peach Bitters*, are prepared by infusion and subsequently strained and clarified by the addition of small quantities of

¹ *Ber.*, 1910, 43, 1430.

isinglass, albumin, etc. König gives the following analyses of various liqueurs :—

Liqueurs.	Specific gravity.	Alcohol by volume.	Extract.	Cane sugar.	Ash.
Absinthe	0·9116	58·9	0·8
Angostura	0·9540	49·7	5·85	4·16	...
Anisette de Bordeaux	1·0847	42·0	34·82	37·44	0·040
Benedictine	1·0709	52·0	36·00	32·57	0·043
Chartreuse	1·0799	43·2	36·11	34·35	...
Crème de Menthe	1·0447	48·0	28·28	27·63	0·068
Curaçao	1·0300	55·0	28·60	28·50	0·040
Ginger	1·0481	47·5	27·79	25·92	0·141
Kümmel	1·0830	33·9	32·02	31·18	0·058

Absinthe contains a variable proportion of alcohol and a considerable amount of volatile essential oils, such as the oils of angelica, anise, cinnamon, cloves, fennel, hyssop, peppermint, etc. The characteristic constituent is oil of wormwood (*Artemisia absinthium*). Absinthe becomes cloudy on addition of water owing to the presence of essential oils. The total essential oils vary somewhat largely in amount. Absinthe containing more than 3·50 g. of total essential oils or more than 1 g. of oil of wormwood per litre is not allowed to be sold for consumption in France, but according to Wynter Blyth, the liqueur as consumed in England may contain as much as 2·52 per cent. of essential oils together with 0·33 per cent. of oil of wormwood.

Chlorophyll is the usual colouring matter, but other vegetable dyes, coal tar colours and copper sulphate are stated to have been met with. Gum benzoin, guaiacum, and colophony appear also to have been used to produce milkiness on dilution.

The toxic effects of absinthe have been ascribed to the presence of thujone (tanacetone), a ketone isomeric with citral. Cuniasse has given a test for thujone which has been modified by L. Duparc and A. Monnier¹ and which depends on the red coloration given by this ketone with sodium nitroprusside. Inasmuch, however, as thujone is a constituent of several essential oils, and the reaction is also given by acetone, carvone, citral and certain other ketones (*cf.* Legal's nitroprusside test for acetone), it is obvious that the test has a very limited value. On the other hand, if a negative result is obtained, the absence of oil of wormwood may be inferred.

The essential flavouring material of *Crème de Menthe* is oil of peppermint, and of *Kümmel*, caraway seeds. *Maraschino* was originally prepared from wild cherries, but other flavouring ingredients are now commonly used, such as bitter almonds, peach kernels, raspberries, etc. It has been stated that as many as two hundred different

¹ *Ann. Chim. anal.*, 1908, 13, 378.

ingredients are used in the preparation of *Chartreuse*. The essential principle of most *Bitters* is gentian, but occasionally agaric, gamboge, senna, rhubarb and aloes are met with. I. Dragendorff¹ has given a scheme for the detection of bitter substances which is primarily intended for hop substitutes in beer, but may also be applied to liqueurs.

1. The Estimation of Sugar in Liqueurs, etc.

The majority of liqueurs contain cane sugar as a sweetening agent. In liqueurs of a comparatively high alcoholic content, the cane sugar must be partially inverted in order to prevent crystallisation from the solution. This inversion is usually effected by boiling either with citric or tartaric acid.

Starch glucose is unsuitable for addition to liqueurs, owing to its content of dextrin, which is liable to cause cloudiness in the liquid. Cane and invert sugar may be estimated in the usual way by copper reduction and polarisation, the following additional points being observed. For a copper estimation the alcohol must be previously removed. The sample should be neutralised, if acid, and the alcohol distilled off, the residue being made up again to the original volume. It is clarified if necessary with basic lead acetate or alumina cream and the excess of lead removed from the filtrate by sodium sulphate. For a polarimetric estimation it is unnecessary to remove the alcohol. If the sample gives no reduction when tested with Fehling's solution, thus showing the absence of invert sugar, the percentage of cane sugar may be ascertained directly with sufficient accuracy by the polarimeter.

If invert sugar is present, the alcohol must be removed by evaporation before a polarimetric reading can be taken. The sample is evaporated on the water-bath after neutralising with ammonia, the residue taken up with water and divided into two portions. The one portion is polarised direct and the other after inversion, both solutions being previously decolorised with basic lead acetate or alumina cream.

The methods for the estimation of sugars are fully described in the section on "Sugar," this Vol., pp. 542 *et seq.*

Glycerol is estimated in liqueurs after removal of the alcohol by the methods given in the section on "Wine," this Vol., p. 766.

Artificial Sweetening Agents such as *Saccharin*, *Dulcine*, etc., are detected and determined by the methods given in the section on "Wine" (this Vol., pp. 780 and 794).

¹ *Z. anal. Chem.*, 1874, 13, 67.

2. Colouring Matters.

In Germany the following colours are allowed to be used in liqueurs and bitters:—

Red. Cochineal, carmine, madder, beetroot, and cherry juices.

Yellow. Saffron, safflower, curcuma, and marigold.

Green. Chlorophyll and mixtures of yellow and blue colours.

Blue. Indigo, litmus, and fruit juices.

Brown. Caramel and liquorice.

In addition to the above purely vegetable colours, aniline dyes are used to a considerable extent. Methods for the detection of aniline dyes are given in the section on "Organic Dyes," Vol. II., pp. 1046 *et seq.*

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VINEGAR.¹

By G. CECIL JONES, A.C.G.I.

Introduction.

IN Germany what may be sold as vinegar, with or without qualification, is the subject of an Imperial ordinance. In the United States also, and in some British colonies, vinegar and some of its more important varieties, such as malt vinegar and cider vinegar, have been defined by law; but in Great Britain the manufacture of vinegar is subject to no control, and its sale is regulated only by the provisions of the Food and Drugs Acts, which make it an offence to sell to the prejudice of the purchaser any article of food which is not "of the nature, substance, and quality demanded" by such purchaser. What that may be in the case of vinegar is so difficult a question to decide, that the promulgation of official definitions abroad, and the demand in certain quarters for similar measures here, is readily understandable.

Formerly it was not permissible for a chemist and druggist to sell as vinegar a fluid containing less than 5 per cent. of acetic acid, but vinegar has disappeared from recent editions of the Pharmacopœia, and in any case the amount of vinegar bought from the druggist must be negligible. It is still often stated that it is permissible to add 0.184 per cent. of sulphuric acid to vinegar, and the opposite statement that this permission has been withdrawn and that it is now illegal to add mineral acid is also met with. The first statement is certainly incorrect, and the second open to doubt. The old Statute (58 George III., cap. 65, xxv.) permitted the addition of sulphuric acid "in proportion not exceeding one thousandth part thereof by weight" (not measure). The permission was given in response to representations that such an addition conferred stability on the vinegar, and it was mainly, if not wholly, for revenue purposes that a limit was assigned to the amount which might be added, vinegar being then an excisable article. In 1844, however, when the excise duty on vinegar was

¹ This section, as stated in the Preface, has been completely rewritten for the English edition. The corresponding section in the German edition is contributed by Dr G. Schüle.

removed, this permission became meaningless and ceased to exist on the repeal, in 1861, of the section of the Act relating to it.

Dilute solutions of acetic acid, with their colour, odour, and flavour more or less modified by traces of other substances derived from the principal raw materials, or produced during manufacture or storage, or occasionally added as such, are sold in Great Britain under the following designations:—

Vinegar (without further qualification),
Malt Vinegar,
Wine Vinegar, White Wine Vinegar, Orleans Vinegar,
Distilled Vinegar, Crystal Vinegar,
Wood Vinegar.

The fluid sold as *Vinegar Essence* (to be distinguished from, the German *Essigessenz*, which is 80 per cent. chem. pur. acetic acid) usually contains 25-30 per cent. (occasionally 60 per cent.) of acetic acid, most of which appears to be derived from refined pyroligneous acid.

Cider Vinegar, which is the principal variety of vinegar in the United States, if made any longer in Great Britain, or imported, does not appear to be sold as such.

Spirit Vinegar is made from potato or grain spirit. It cannot be made profitably in Great Britain owing to the duty on alcohol, but is imported in small quantities from Germany. It is a strong vinegar, containing upwards of 12 per cent. of acetic acid, and one of its uses in this country appears to be to serve as a basis for a factitious wine vinegar.

Artificial Vinegar is a variety yet unknown in Great Britain, but it is not improbable that it may become the compulsory designation of vinegar of the type hereinafter referred to as wood vinegar (see p. 744).

Vinegar (without further qualification). By far the largest quantity of vinegar sold in Great Britain is sold either as vinegar, without further qualification, or as malt vinegar.

There is a large trade in an article made by diluting 80 per cent. acetic acid to vinegar strength, colouring it with caramel, and generally blending it with a little malt vinegar; also, many manufacturers of fermentation vinegar "fortify" their produce with acetic acid. The acetic acid used in such cases, though a highly refined article, is usually derived from the destructive distillation of wood, and not from alcohol, by acetous fermentation. The term "fortification" is misleading, as it is usually followed by dilution of the vinegar to a lower strength than it had before the addition of acetic acid. Weak vinegars do not keep well, and of two vinegars of equal acid strength, that made from a fortified vinegar will keep better, as it contains a smaller proportion of

the minor constituents of fermentation vinegar, which are favourable to the development of micro-organisms.

In regard to the acid strength of vinegar, five numbered grades are known in the trade as No. 24, No. 22, No. 20, No. 18, and No. 16 vinegar. Originally these numbers were intended to indicate the number of grains of sodium carbonate which would neutralise one ounce of the vinegar in question, and on this basis a No. 16 vinegar should contain approximately 4.1 per cent. of acetic acid. As a rule vinegar sold as No. 16 does in fact contain at least 4 per cent. of acetic acid, but that sold as No. 24 frequently contains less than 6 per cent., and makers seem to hold themselves free to give any significance they please to the marks employed. Probably, however, no vinegar containing less than 5.5 per cent. of acetic acid is sold as No. 24. In addition to the numbered grades, most makers sell a vinegar containing 3.5 per cent. of acetic acid (rarely less), which they designate as "Diamond" or "Double Diamond."

Mineral acid is probably never now added to brewed vinegars. Copper, in serious quantity, has been found in vinegar, even in quite recent years, but modern plant must tend to reduce the probability of such occurrences in future. Arsenic is always present in vinegar made from malt of British manufacture, but very rarely in amount approaching $\frac{1}{100}$ gr. per gallon. On the other hand, though glucose manufactured for sale in England is substantially free from arsenic, some vinegar makers make their own glucose, and the introduction of a serious trace of arsenic by the use of impure sulphuric acid in the converter is a possibility not to be overlooked. The same thing might occur where sulphuric acid was added to the vinegar itself. Colouring matters other than caramel are rarely used. In regard to preservatives, calcium bisulphite is much used and salicylic acid occasionally.

Malt Vinegar might be expected to be the product of the alcoholic and acetous fermentation of malt wort, but this is seldom the case. If derived wholly from cereals, the starch of which has been saccharified by the diastase of malt, not more than 10 per cent. of the raw material need be malt, and probably all the vinegar of this class is sold as malt vinegar, as well as much that is largely derived from commercial glucose or from starchy materials hydrolysed by means of sulphuric acid in the vinegar works itself. Raw sugar and molasses are also used, and other vinegars prepared by saccharification with diastase are often "fortified." Finally diluted acetic acid, coloured with caramel and blended with less than an equal bulk of fermentation vinegar is sometimes, but rarely, sold as malt vinegar.

Wine Vinegar (White Wine Vinegar, Orleans Vinegar) should be the product of the acetous fermentation of genuine grape wine. Since genuine wines vary in alcoholic strength and manufacturing losses also

vary, continental authorities are mostly content with an acetic acid content of 5 per cent. or a little more. This may possibly explain the fact that wine vinegar containing as much as 6 per cent. of acetic acid rarely comes on the market now, though formerly the average was higher than this. Imitation wine vinegar is made by diluting spirit vinegar, colouring it and treating it with wine lees, and distilled vinegar is also sold as white wine vinegar, but the product could scarcely be mistaken for the latter.

Distilled Vinegar (Crystal Vinegar) is understood to be prepared by the distillation of malt vinegar. A genuine distilled vinegar is about 10 per cent. weaker than the vinegar from which it is made. Before distillation vinegar is sometimes fortified until it contains over 10 per cent. of acetic acid, but even in such cases it is usual to dilute the distillate to approximately 5 per cent. strength.

Wood Vinegar is the name given to a product which owes its acetic acid largely to refined pyroligneous acid. Such vinegar, as well as fortified vinegar, may possibly in future be required to be described as "Artificial Vinegar."

A.—THE ANALYSIS OF THE RAW MATERIALS OF THE VINEGAR INDUSTRY.

1. Malt.

In malt the extract, diastatic power, and arsenic should be estimated. The extract and arsenic should be determined as described in the section on "Brewing Materials and Beer" (this Vol., pp. 809 and 836), but, in the determination of the diastatic power of vinegar malts by Ling's method (see p. 812), not more than 1 c.c. of the 5 per cent. extract should be added to the solution of soluble starch. To the manufacturer of all-malt vinegar, the value of a malt will depend mainly on the extract it yields, but a grain vinegar maker may attach more importance to the diastatic power. As malt can readily be produced with less than $\frac{1}{400}$ gr. of arsenic per pound, it is reasonable to specify that it shall not contain more than $\frac{1}{300}$, and to refuse delivery if it contains more than $\frac{1}{200}$ gr. per pound. This is a safe figure, but leaves no large margin of safety in the case of strong all-malt vinegar. Where but little malt is used, a less stringent specification might seem to be permissible, but is not in fact justifiable unless the other materials used are known to be wholly free from arsenic.

2. Barley, Rice, Rice Grits, Maize Grits.

The value of these materials to the vinegar maker is measured most exactly by their content of starch, as determined by one or other

of the modifications of Lintner's polarimetric method (see section on "Starch," this Vol., p. 667).

3. Flaked Maize.

The comparatively high price of this material is only justified in proportion as its starch has been rendered readily amenable to the action of malt diastase. It should be valued, therefore, not on its starch-content, but on the extract it yields when mashed with cold water malt extract, as described under "Brown Malts" in the section on "Brewing Materials and Beer" (p. 817).

4. Glucose.

Commercial glucose should be analysed as described in the section on "Brewing Materials and Beer" (this Vol., pp. 824 *et seq.*), except that the "unfermentable matter"—to which some importance attaches—should be determined by a method which takes account of the fact that vinegar brewers usually ferment their worts in presence of active malt diastase. The solution to be fermented should have added to it 5-10 per cent. of 40 per cent. cold water malt extract as well as yeast. The results should be corrected for this addition by running a control experiment with an equal amount of cold water malt extract, water, yeast, etc., but without glucose. Where glucose vinegar, without the use of malt, is to be made, the unfermentable matter should, of course, be determined according to the ordinary methods of sugar analysis. Glucose of British manufacture is usually remarkably free from arsenic, but the determination should never be omitted.

5. Raw Sugars, Invert Sugar, Molasses.

These materials should be analysed as described in the section on "Sugars" (pp. 542 *et seq.*), except that the unfermentable matter should be determined as described above under Glucose. Molasses are often relied on to bring the gravity of an otherwise thin vinegar up to some standard adopted by the maker, so that the accurate determination of unfermentable matter may be of the first importance. Invert sugar is too costly to find economic employment in vinegar works, but if used, as it is sometimes said to be, should be tested for arsenic.

6. Acetic Acid.

This should be of the grade known as 80 per cent. chem. pur., and in addition to being tested for strength, should be examined for the presence of mineral acid, heavy metals, especially copper, and for empyreumatic substances which might affect the odour or flavour of the vinegar. The strength is most conveniently determined by

taring a stoppered weighing-bottle containing about 10 c.c. of water, adding 3 c.c. of the acid, again weighing, rinsing into a flask with water free from carbon dioxide, and titrating with $N/1$ alkali hydroxide, using phenolphthalein as indicator.

For the detection and estimation of *Mineral Acid* 5 c.c. of the acetic acid is diluted to 100 c.c. with water, and 10 c.c. of the diluted liquid is mixed with 10 c.c. of alcohol, and one drop of a solution of methyl orange (0.5 g. per litre), and titrated with $N/10$ alkali. If any considerable amount of alkali is required, a second titration should be made with a somewhat larger amount of alcohol present, namely, 10 c.c. *plus* one-third the volume of $N/10$ alkali used in the first titration, and, as in all exact work with methyl orange, the end-point (a clean yellow not changed by further addition of alkali) is best determined by reference to the tint of a control solution, equal in volume to that of the fully titrated liquid, and containing one drop of the indicator. P. Schidrowitz,¹ who first described the method, used distilled water as control liquid, but an over-titrated portion of the liquid to be analysed is an even better control, and allows of the application of the method to very pale but not quite colourless vinegars.

For the detection of acid unsuitable for vinegar making by reason of the presence of more than negligible traces of certain empyreumatic substances, a test based on the use of permanganate, the consumption of which should be small, is often recommended. According to G. Schüle,² 5 c.c. of acid mixed with 15 c.c. of water should not decolorise 1 c.c. of 1 per cent. potassium permanganate solution in ten minutes. Acid which would not withstand this test would scarcely be sold on the English market as "chem. pur." A very much more stringent permanganate test would doubtless exclude the occasional consignments of acid which is unsuitable for vinegar making, but if stringent enough to ensure this, would probably exclude much acid of good quality. Acetic acid intended for vinegar making should be broken down to vinegar strength, smelt and tasted, neutralised, again tasted, warmed, and again smelt. On this test alone, or on the first part of it, it is possible, with experience, to decide whether a particular sample or consignment is fit for vinegar making. As a further test, a portion of the sample should be evaporated to dryness in a porcelain dish over a free flame, and another portion mixed with an equal bulk of concentrated sulphuric acid. A considerable black residue in the first experiment, and a dark brown solution in the second, will nearly always be obtained in the case of samples which may have been condemned as the result of a "nose" test. 80 per cent. chem. pur. acid could not be bought at the ordinary price to a specification which required it to leave no residue on evaporation, and to give no colour when mixed

¹ *Analyst*, 1903, 28, 233.

² German Edition, Vol. IV., p. 224.

with sulphuric acid, as the general run of acid develops a yellow or pale brown colour with sulphuric acid, and, on evaporation, leaves a slight residue which chars on further heating; but acid can be bought to sample, and the above tests should always be made simultaneously on the sale sample and on the sample taken from the delivery. Acid sold as "chem. pur." does not contain furfural or sulphur dioxide, which are present in lower grades.

7. Caramel.

The tinctorial power of this material should be determined by dissolving 10 g. in water, making up to 100 c.c., diluting 10 c.c. of this solution to a litre, filtering if necessary, and comparing the colour of the solution, contained in a 1 in. cell, with Lovibond's tintometer glasses of the series known as "52."

8. Sulphuric Acid.

Sulphuric acid for use in converting starch should be free from arsenic and lead. The methods for the estimation of these impurities and for the determination of the acid strength are described in the section on "Sulphuric Acid," Vol. I., pp. 377 *et seq.*

B.—THE ANALYSIS OF VINEGAR.

Results are most conveniently expressed in grams per 100 c.c.

1. The Specific Gravity.

Some makers work to a standard gravity; the number also affords a means of converting results of analysis into percentages by weight, and some analysts consider it of value in deciding on the origin of a particular sample. For all these purposes, a determination by means of a spindle is sufficiently exact.

2. Total Acid.

This is determined by diluting 5 c.c. of vinegar with water free from carbon dioxide, using much water if the vinegar be highly coloured, and titrating with *N*/10 alkali hydroxide, using phenolphthalein as indicator. In the absence of other acids, the acidity is calculated to acetic acid.

3. Alcohol.

200 c.c. of the vinegar is exactly neutralised and distilled until nearly 100 c.c. has been collected. The distillate is made up to exactly 100 c.c. with distilled water, mixed, and its specific gravity taken by means of the specific gravity bottle. As this method will detect 0.005

per cent. of alcohol and estimate larger quantities with an error not exceeding 0.005 per cent., the second distillation usually recommended can, as a rule, be dispensed with. In a works where the estimation is important, as vinegar brewers usually wish to have some unchanged alcohol in their product, there will be no difficulty in getting sufficient vinegar for the test. To the public analyst the figure is of less value, and will usually have to be arrived at by two or more distillations of a small quantity, and the use of a Sprengel tube to determine the specific gravity of the final distillate.

4. Heavy Metals.

Vinegar should be systematically tested for the presence of copper, especially after the introduction of any new plant. For this purpose a considerable volume (200-500 c.c.) is evaporated to dryness and the residue incinerated after the addition of a little sodium hydroxide and potassium nitrate and examined for heavy metals in the usual way.

5. Arsenic.

Arsenic will only be present in negligible proportions in the produce of a works which controls its raw materials by one of the quantitative forms of the Marsh test which have been devised for determining minute amounts of arsenic. (See section on "Sulphuric Acid," Vol. I., pp. 362 *et seq.*) The final product in such cases may, if desired, be systematically controlled in the same way.

6. Cyanogen Compounds.

In vinegar which has been clarified by means of potassium ferrocyanide, there is a risk of hydrogen cyanide being formed if excess of the clarifying agent is used. The excess of ferrocyanide is gradually oxidised to Prussian blue and hydrogen cyanide, more than half the total cyanogen being liberated as hydrogen cyanide; this probably combines with aldehyde, as it cannot be determined or even detected by Feld's method. The amount is never large and it is not known with certainty whether the resulting vinegar is toxic or not, but the appearance of Prussian blue should be immediately followed by a reduction in the proportion of ferrocyanide in use. Even if non-toxic, its distribution would give rise to complaint if the deposition of Prussian blue continued.

C.—THE FURTHER EXAMINATION OF VINEGAR.

The foregoing tests exhaust the technical methods, properly so-called, which are applied to the analysis of vinegar. But for purposes of control on the part of purchasers, a number of other determinations

are made to decide whether the vinegar is up to specification or mis-described. Some of these methods are described in the sequel.

1. Determination of Free Mineral Acid.

In colourless or nearly colourless vinegars this determination may be made by the method of Schidrowitz¹ (p. 746). In coloured vinegars free mineral acid may be determined by titration with alkali using methyl orange paper as indicator. To determine the end-point sharply, it is necessary to use some genuine vinegar or a 5 per cent. solution of acetic acid as a control if it is desired to obtain a tolerably accurate result by a single titration; but, in a second experiment, the liquid from the first determination, to which a distinct excess of alkali has been added, affords the best control. This method is also due to Schidrowitz, and both methods give excellent results with practice. The method for colourless vinegars is empirical and depends on the fact that, within certain narrow limits of concentration of alcohol, acetic acid is without action on methyl orange, whereas sulphuric acid acts normally. If, however, the concentration of alcohol be excessive, sulphuric acid will be under-estimated, and in an extreme case might not be detected at all. The method has been criticised by F. W. Richardson and J. L. Bowen,² who recommend a modification of Hehner's method.

With the exception of the use of hydrogen peroxide, a recent improvement due to Richardson and Bowen, the following is substantially the original method proposed by Hehner.³ For the determination 25 c.c. of vinegar are mixed with 25 c.c. of $N/10$ sodium hydroxide, the mixture is evaporated to dryness, and the residue is charred at a low temperature. The resulting black ash is treated with a little neutral hydrogen peroxide solution (to prevent liberation of hydrogen sulphide), and then with 50 c.c. of $N/10$ sulphuric acid. The mixture is boiled and filtered, the carbonised residue and filter are washed, and the filtrate and washings titrated with $N/10$ alkali, using methyl orange as indicator. In theory, 25 c.c. should be required if the original vinegar was genuine, and any consumption of alkali beyond 25 c.c. is calculated to mineral acid. In practice, genuine vinegars often require less than 25 c.c. in the final titration, and mineral acid, when present, may be under-estimated owing to the presence of normal potassium phosphate in the ash of the vinegar. For this reason, Richardson and Bowen⁴ have proposed to modify the method. An advantage of the method as described lies, however, in the fact that the content of mineral acid cannot be over-estimated; also,

¹ *Analyst*, 1903, 28, 233.

³ *Analyst*, 1876, 1, 105.

² *J. Soc. Chem. Ind.*, 1906, 25, 836.

⁴ *Loc. cit.*

the results are only likely to be substantially too low in the case of malt vinegars, which are rarely, if ever to-day, adulterated with mineral acid.

A. Hilger's method¹ has met with more criticism than approval in Great Britain. In using this method it is most essential to obtain the right indicator, Methyl Violet, 2 B of the Bayer Co., B of some other makers, but easily specified as No. 427 of Schultz and Julius' *Tabellarische Übersicht der künstlichen organischen Farbstoffe* (4th edition, 1902).

2. Fixed Organic Acids.

Oxalic acid may be detected and determined by precipitation with calcium sulphate, but, except that it might be added with deliberate intent to poison, is not likely to be found in vinegar. It would not be an economical adulterant. Tartaric acid is even more costly, but is said to have been found in factitious wine vinegar. To detect it, 200 c.c. or more of the vinegar is evaporated, and the residue, which will be viscous if free tartaric acid is present in quantity, is taken up in alcohol, and the solution filtered and mixed with an alcoholic solution of potassium acetate. If tartaric acid be present, streaks will form on the beaker on stirring with a glass rod, or even a distinct precipitate may separate. Approximately quantitative results can be obtained by titration of the precipitate with standard alkali.

3. Total Solids.

A measured volume of the vinegar is evaporated to dryness, the residue dissolved in water, which is also evaporated, and this procedure again repeated. The residue is finally dried in a steam-oven for two hours, allowed to cool, and weighed. If the re-solution of the first residue be omitted, the solids will be over-estimated, as the residue obstinately retains acetic acid when dried at temperatures not exceeding 100°. ²

4. Ash.

The residue from the preceding determination is charred at a low temperature, and repeatedly extracted with small portions of hot water, which are then decanted through an ashless filter. The filter is returned to the dish, dried and ignited. The filtrate is then added to the contents of the dish, evaporated to dryness, heated to dull redness, allowed to cool in a dessicator, and weighed.

Solubility and Alkalinity of Ash.—In the United States the water-soluble ash from 100 c.c. of malt vinegar is required to contain not less

¹ *Arch. f. Hygiene*, 1888, 8, 448.

² Cf. Brode and Lange, *Arbeit. Kaiserl. Gesundheitsamte*, 1909, 30, 1; Russell and Hodgson, *Analyst*, 1910, 35, 346.

than 9 mg. of P_2O_5 , and to neutralise not less than 4 c.c. of *N*/10 acid. A. C. Chapman¹ has shown that genuine malt vinegar may fail to comply with the first of these requirements, and it may also fail to comply with the other. To carry out the test the vinegar is evaporated to dryness, the residue charred at a low temperature, extracted with hot water, the extract filtered and used for the determinations.

5. Total Phosphoric Acid.

More importance attaches to this constituent, the determination of which in vinegar presents no special difficulty beyond those common to all determinations of phosphorus in substances containing organic matter; but as many of the methods recommended for the purpose are both troublesome and untrustworthy, reference may be made to the method of Plimmer and Bayliss,² or to Neumann's³ method, on which it is based.

6. Nitrogen.

For this estimation 25 c.c. of the vinegar are evaporated to a syrupy consistency, and the nitrogen determined by Kjeldahl's method. The results are best expressed as grams of nitrogen per 100 c.c., and not calculated to proteins by means of an empirical factor.

7. Potassium Hydrogen Tartrate.

Wine vinegar usually contains about 0.2 per cent. of tartar. Its presence may be detected by evaporating 100 c.c. to dryness, and treating the residue with alcohol; tartar remains undissolved. To prove its identity, the alcohol is poured off, and the residue dissolved in a small quantity of hot water; on cooling the aqueous solution and rubbing the sides of the vessel with a glass rod, potassium hydrogen tartrate will be deposited in streaks. An addition of an equal bulk of alcohol makes the reaction more delicate.

8. Foreign Pungent Materials.

According to some authorities, cayenne pepper, ginger, and the like are sometimes added to vinegar. Though present in compounded condiments sold under special names, they are probably not added to vinegar intended to be sold as such in this country. If present in quantity sufficient to affect the flavour of the vinegar, the neutralised and concentrated vinegar will possess a flavour sufficiently pronounced to prove sophistication of some kind beyond doubt, but it will rarely be possible to identify the added substance.

¹ *Analyst*, 1912, 37, 123.

² *J. Physiology*, 1906, 33, 439.

³ *Z. physiolog. Chem.*, 1902, 37, 129.

9. Polarisation.

Malt vinegar intended for export to the United States must polarise to the right. Some genuine malt vinegars are lævo-rotatory.¹

10. Preservatives.

Sulphur dioxide, which may exist either as such or combined with aldehyde, may be determined as follows:—50 c.c. of the vinegar is mixed with 100 c.c. of approximately *N*/1 alkali hydroxide to decompose the aldehyde compound, and after standing fifteen minutes, with occasional shaking, is made strongly acid by addition of about 15 c.c. of phosphoric acid (sp. gr. 1.7), and distilled in a current of carbon dioxide, the distillate being received in a vessel containing *N*/10 iodine solution, into which the end of the condenser should dip. When about 75 c.c. of distillate has been collected, the sulphuric acid resulting from the oxidation of the sulphur dioxide by iodine is determined as barium sulphate. Volumetric methods are insufficiently exact when the permissible limit of sulphur dioxide is very low, as in the case of vinegar intended for importation into the United States.

Salicylic acid is extracted with ether after addition of a few drops of sulphuric acid, and detected, and if necessary estimated in the usual manner (*cf.* the section on "Organic Preparations," this Vol., p. 385). As genuine wine vinegar may contain a trace of salicylic acid, not more than 50 c.c. should be taken for the test; the small quantity which might be present naturally will not be detected in 50 c.c.

Other preservatives are seldom, if ever, added to British vinegar, but benzoic acid has often been used in other countries, and, more rarely, boric acid and formaldehyde.

11. Foreign Colouring Matters.

Caramel alone appears to be used, and is unobjectionable. If a chemist is required to decide whether a consignment of vinegar complies with a specification forbidding the addition of caramel, he must assure himself that any method adopted for its detection will in fact detect it if present, and give a negative result in its absence. Most of the methods described for the purpose fail in one or other respect and some in both.² Modern preparations of caramel differ among themselves, but are all very different from the "burnt sugar" formerly sold.

¹ Chapman, *Analyst*, 1912, 37, 123.

² *Cf.* Schidrowitz, *J. Soc. Chem. Ind.*, 1902, 21, 816.

12. Aldehyde, Glycerol, Dextrin, Fixed and Volatile Acid.

These are sometimes determined, and more rarely *Malic Acid*. Aldehyde may be determined by neutralising 100 c.c. of the vinegar, distilling 10 c.c., and treating the distillate as described in the section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., p. 725. Glycerol, dextrin, and malic acid may be determined as described in the section on "Wine," this Vol., pp. 766, 782, and 790. An indirect method is generally recommended for fixed acid, but to have any value the determination should be a direct one.¹

Detection of Misdescription.

As a preliminary to forming a judgment concerning vinegar, the ash, phosphoric acid, and nitrogen are often calculated to parts per 100 parts "original solids," as recommended by Hehner. The amount of original solids is an empirical number obtained by multiplying the acetic acid percentage by 1.5 and adding the result to the percentage of total solids present in the finished vinegar, and is based on the supposition that the acetic acid has been derived from glucose without loss. Having regard to the comparatively wide limits within which even genuine malt vinegar varies, there appears to be no justification for the trouble involved in these calculations. In the sequel, vinegars of 5 per cent. acetic acid content are to be understood. Stronger malt vinegars contain, on the average, more ash, phosphoric acid, and nitrogen, and weaker ones less; but some of the averages given may be 20 per cent. in error, and the minima are only the minima which have been recorded.

Vinegar made wholly from malt and barley seldom contains less than 2 per cent. of total solids, but the figure may go as low as 1.2 per cent. For export to the United States as malt vinegar it must not contain less than 2 per cent. The average is probably about 2.2 per cent. The ash varies from 0.2 to 0.5 per cent. The average content of phosphoric acid calculated as P_2O_5 is probably about 0.08 per cent., and though no lower figure than 0.05 per cent. has been recorded, there is a growing tendency to eliminate as much phosphoric acid (and protein) as possible, with a view to improving the keeping qualities of the vinegar, and the limit may not have been reached. The content of nitrogen varies from 0.07 to 0.10 per cent.

When vinegar is made largely from maize grits saccharified by a small quantity of malt, and such vinegar is generally regarded as entitled to be called malt vinegar, the phosphoric acid may in an

¹ Further information on the analysis of vinegar may be found in a paper by Brode and Lange, *Arbeit. Kaiserl. Gesundheitsamte*, 1909, 30, 1-54.

extreme case sink to 0.02 per cent., and is quite commonly under 0.05 per cent. The nitrogen also may fall to 0.05 per cent.

Other fermentation vinegars may contain as little as 0.015 per cent. of P_2O_5 or of nitrogen. The total solids and ash are seldom below the minimum recorded for malt vinegars. Some sugar vinegars can be recognised by their low nitrogen-content as certainly not derived wholly from cereals saccharified by diastase, but other vinegars made mainly from rice hydrolysed by acid contain as much nitrogen as malt vinegars, and though their content of P_2O_5 is low (0.015-0.020), they cannot be distinguished with certainty from vinegar made from maize grits saccharified by diastase.

But there is a large amount of vinegar sold containing about 0.5 per cent. of total solids, 0.05 per cent. of ash, and 0.003 per cent. of P_2O_5 and of nitrogen. Such vinegar cannot be mistaken for malt vinegar or for a fermentation vinegar produced from any of the materials which could be economically employed in this country. It is in fact made by diluting acetic acid, colouring with caramel, and blending with a little vinegar bought as malt vinegar, but itself often a misdescribed article. Some vinegars of this class contain solids, ash, phosphoric acid, and nitrogen in proportions considerably exceeding those given, but rarely enough to leave any doubt as to their origin. On the other hand, fortified vinegars, that is to say, vinegars consisting mainly of brewed vinegar with a small addition of acetic acid, cannot be detected, the methods described in some text-books for the determination of empyreumatic substances being quite useless to-day, owing to the degree to which the refinement of acetic acid is carried.

Wine vinegar is characterised by the presence of potassium hydrogen tartrate. Continental authorities usually require it to have at least 1 per cent. of total solids and 0.1 per cent. of ash. The total solids average 2 per cent., and 1.1 per cent. appears to be the lowest figure recorded. A trained nose is of value in examining wine vinegar, as in all vinegar work; the neutralised as well as the original vinegar should be smelt.

LITERATURE.

Local Government Board Report, "On the Preparation and Sale of Vinegar in Relation to the Administration of the Sale of Food and Drugs Acts," by J. H. HAMILL, Report No. 5 of Inspector of Foods, 1908.

WINE

By Prof. K. WINDISCH, Ph.D., Director of the Technological Institute of the Royal Agricultural High School, Hohenheim. English translation revised by P. SCHIDROWITZ, Ph.D.

Prefatory Note.

THE judging of wine and the interpretation of analytical results in Germany are based upon a "Food Law" of 1879 and a "Wine Law" of 1909, in association with official instructions for the examination of wine, issued on 25th June 1896; these instructions include the majority of the most important methods for the analysis of wine.

There is no special "Wine Law" in the United Kingdom. Wine, like other articles of food and drink, can be dealt with either under the "Food and Drugs Act" or under the "Merchandise Marks Act." Adulteration in the narrower sense of the term is not very common nowadays, and occurs more frequently in the case of non-alcoholic or "temperance" wines than with ordinary wines. In the case of "non-alcoholic" wines, the analyst should direct his attention chiefly to the detection and determination of preservatives, such as salicylic acid, boric acid, boro-fluorides, boro-glycerides, contamination with metallic impurities (arsenic, copper, lead), and to the presence of artificial dye-stuffs. In the case of natural wines, preservatives (particularly salicylic acid and boro-compounds) are occasionally found, but this is rarely the case. Most natural sound wines, containing upwards of 12 per cent. of alcohol, do not, given reasonable conditions of cellar treatment, etc., require either fortification or the addition of preservatives in order to keep them from deterioration. It occasionally happens that an excess of sulphurous acid (particularly in the case of sweet or semi-dry, non-carbonated white wines) is present as a result of excessive sulphuring during the racking operations; and in the case of sherries an excessive amount of sulphate—the result of over-plastering—may be found. The German wine law in regard to these and similar matters may be taken as an excellent guide by the analyst in the United Kingdom, subject to his bearing in mind the fact that the data on which it is based are mainly derived from observations in connection with German wines. With a view to the proper interpretation of

results, therefore, the statistical wine literature should always be consulted in case of doubt. A very large number of results will be found tabulated in *Chemie der menschlichen Nahrungs-u.-Genuss mittel*, by J. König (4th edition, 1903-10), and in *Vins*, by Gayon and Laborde (1912). In this latter work full details are given of the official French regulations and methods of analysis for the examination of wines.

Other adulterations that may occasionally occur in wines are the addition of artificial sweetening agents, such as saccharin, and of "essences" for the purpose of imparting a specific flavour in imitation of a natural wine; but broadly speaking such adulterations are rare. On the other hand, misdescription is by no means uncommon; for instance, a liquor made by fermenting a concentrated Greek or Sicilian "must" in London may be passed off as French claret or Bordeaux, or even under the name of a specific growth. Fraud of this kind is, however, very difficult to detect by analysis.

The analysis of wine should not be regarded solely as a means of detecting adulteration or misdescription; it may, if rationally employed, be of considerable utility to the shipper or merchant from the point of view of judging quality and development.

In accordance with the above statement the following description of the methods employed in the analysis of wines comprises the official regulations in force in Germany, together with explanatory notes, as given in the German edition, an account of other methods of analysis, and a concluding description of the judging of wines on the basis of chemical analysis.

I. THE ANALYTICAL EXAMINATION OF WINE.

A.—THE DRAWING, LABELLING, STORAGE, AND DISPATCH OF SAMPLES OF WINE FOR CHEMICAL ANALYSIS, AND GENERAL REMARKS. (GERMAN REGULATIONS.)

1. From every wine intended for chemical examination a sample of at least $1\frac{1}{2}$ litres is to be drawn. This quantity is sufficient for the tests usually required. The quantity necessary for any further tests depends upon the nature of these tests.

2. The bottles and corks used must be quite clean. Stoneware or other opaque bottles, in which any dirt cannot be seen, must not be used.

3. Each bottle must be provided with an arrangement for preventing unauthorised opening, and with an adhesive label, on which are noted details of the identity of the sample. In addition, the size of the barrels, the extent to which they are filled, and the condition of the

wine, are to be given separately; the extent of the formation of mould, if any, is to be particularly observed.

4. The samples are to be forwarded to the testing station as soon as drawn; if an early dispatch is impossible, they must be kept lying down in a cool place protected from sunlight. Special promptitude in forwarding samples of new wine is necessary on account of the ease with which it undergoes alteration.

5. For the valuation of a wine the tests and estimations are usually to be applied to the following properties and constituents of each sample:—

- (1) Specific gravity.
- (2) Alcohol.
- (3) Extract.
- (4) Mineral constituents.
- (5) Sulphuric acid, in red wines.
- (6) Free acids (total acid).
- (7) Volatile acids.
- (8) Non-volatile acids.
- (9) Glycerol.
- (10) Sugar.
- (11) Rotatory power.
- (12) Impure glucose (qualitative).
- (13) Foreign colouring matters (in red wines).

In special circumstances the tests and estimations are to be extended to the following constituents:—

- (14) Total tartaric acid, free tartaric acid, tartar and alkaline earth tartrates.
- (15) Sulphuric acid, in white wines.
- (16) Sulphurous acid.
- (17) Saccharin.
- (18) Salicylic acid (qualitative).
- (19) Gum and dextrin (qualitative).
- (20) Tannin.
- (21) Chlorine.
- (22) Phosphoric acid.
- (23) Nitric acid (qualitative).
- (24) Barium.
- (25) Strontium.
- (26) Copper.

The results of these tests are to be given in the order mentioned. Where constituents of wine not mentioned in the list are found or determined, the method employed must in all cases be given.

6. As normal temperature, 15° is prescribed; all measurements on wine are to be carried out at, and all results are to refer to this temperature. Turbid wines must be filtered before analysis; if their temperature is below 15° , they are to be warmed to 15° with the undissolved portion, and shaken before filtration.

7. The quantities of the constituents of the wine are to be expressed as weight in grams of the constituent in 100 c.c. of the wine at 15° .

Note.—It is important to record the extent to which the barrels are filled, since in wines kept in not completely filled barrels micro-organisms easily settle, and alter the composition of the wine, in particular the vinegar bacterium (*Bacterium aceti*) and mould (*Mycoderma vini*).

The external condition of the wine often gives indications of disease. Turbidity may be caused by yeast cells, by other organisms (acetic acid producing organisms, moulds, bacteria in wine which has soured, etc.), or by the separation of certain constituents, such as tartar, calcium tartrate, colouring matter, etc. The nature of the turbidity may be recognised under the microscope. The substances causing turbidity are separated either by allowing them to settle in a conical precipitating glass, or by centrifuging or filtering the wine.

B.—OFFICIAL METHODS OF ANALYSIS. (GERMAN REGULATIONS.)¹

1. Determination of the Specific Gravity.

The specific gravity of the wine is, according to the official regulation, to be carried out by means of a pycnometer. A simplification of the calculation has been given by F. Bolm.² In examinations other than for legal purposes, the specific gravity may be determined by means of an accurate, tested, Westphal (Mohr) balance, or with hydrometers having sufficiently fine divisions. It is only for wines with more than 4 g. of extract per 100 c.c. that the accurate determination of the specific gravity is of great importance, because for these wines it is used to determine the extract.

2. Estimation of the Alcohol.

The wine in the pycnometer, used for the specific gravity determination, is transferred to a distilling flask of 150-200 c.c. content, and the pycnometer rinsed out three times successively with small quantities of water. A small quantity of tannin is placed in the flask to prevent foaming, and the flask is then connected by means of a rubber stopper and bulb-tube to a Liebig condenser; the pycnometer in which the wine was measured is used as a receiver. Distillation is carried on

¹ These Regulations are given in full where necessary. The explanatory notes are added as Notes at the end of the description of the Official Method of Analysis.

² Z. Unters. Nahr. u. Genussm., 1900, 3, 667.

until about 35 c.c. of liquid have come over; the pyknometer is filled nearly to the neck with water, the contents mixed by a whirling motion until layers of different densities can be no longer seen, and the pyknometer kept for thirty minutes in a water-bath at 15°. Water is carefully added from a capillary tube until the lower edge of the surface of the liquid just touches the mark. After drying the empty part of the pyknometer with small rolls of filter paper it is weighed, and the specific gravity of the distillate thus determined. The number of grams of alcohol per 100 c.c. of wine corresponding to this specific gravity is then ascertained by means of the Table given in the section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., p. 711.

In the case of diluted wines the alcohol is to be given in percentage by volume.

Note.—Small quantities of volatile acids go over into the distillate with the alcohol; with normal wines their quantity is so small that they do not noticeably affect the specific gravity of the distillate. In the case of some wines containing much acetic acid, it is necessary to neutralise the wine before distillation.¹ Sweet wines containing much extract must not be distilled too far, since the residue from the distillation easily burns.

For non-legal analysis the content of alcohol of the distillate made up to the original volume may be determined by means of an accurate alcoholometer. The special forms of apparatus suggested for determining the alcohol without distillation, such as the vaporimeter, the ebullioscope, the liquometer (capillarimeter), the drop counter (stalagmometer), and also the refractometric and the cryoscopic methods, are not to be recommended, as they are uncertain. The same applies to the indirect determination of the alcohol from the specific gravities of the original and the de-alcoholised wine.

3. Estimation of the Extract (Content of Extractives).

Extract (total content of extractives) consists of the originally dissolved constituents of the completely fermented wine after removal of the alcohol and water.

Since the method to be chosen for the estimation of the extract depends upon the amount of extract, the value of x is first calculated from the formula:—

$$x = 1 + S - S_1$$

in which S is the specific gravity of the wine (estimated as in No. 1), S_1 the specific gravity of the alcoholic distillate from the wine made up to the original volume (estimated as in No. 2).

The value E , corresponding to the value of x , is taken from the following Table prepared by K. Windisch.

¹ C. Amthor, *Z. Unters. Nahr. u. Genussm.*, 1898, 1, 811; P. Kulisch, *Ber. der landw. Versuchstation Colmar i. Els.*, 1904-1906, p. 81.

Table 60.

Table for the Determination of E, which governs the choice of Method to be used for the Estimation of the Extract in Wines. (K. Windisch.)

x.	E.	x.	E.	x.	E.	x.	E.	x.	E.
1.0000	0.00	1.0100	2.58	1.0200	5.17	1.0300	7.76	1.0400	10.35
2	0.05	2	2.63	2	5.22	2	7.81	2	10.40
4	0.10	4	2.69	4	5.27	4	7.86	4	10.45
6	0.15	6	2.74	6	5.32	6	7.91	6	10.51
8	0.20	8	2.79	8	5.38	8	7.97	8	10.56
1.0010	0.26	1.0110	2.84	1.0210	5.43	1.0310	8.02	1.0410	10.61
2	0.31	2	2.89	2	5.48	2	8.07	2	10.66
4	0.36	4	2.94	4	5.53	4	8.12	4	10.71
6	0.41	6	3.00	6	5.58	6	8.17	6	10.76
8	0.46	8	3.05	8	5.64	8	8.22	8	10.82
1.0020	0.52	1.0120	3.10	1.0220	5.69	1.0320	8.27	1.0420	10.87
2	0.57	2	3.15	2	5.74	2	8.33	2	10.92
4	0.62	4	3.20	4	5.79	4	8.38	4	10.97
6	0.67	6	3.26	6	5.84	6	8.43	6	11.03
8	0.72	8	3.31	8	5.89	8	8.48	8	11.08
1.0030	0.77	1.0130	3.36	1.0230	5.94	1.0330	8.53	1.0430	11.13
2	0.82	2	3.41	2	6.00	2	8.59	2	11.18
4	0.87	4	3.46	4	6.05	4	8.64	4	11.23
6	0.93	6	3.51	6	6.10	6	8.69	6	11.28
8	0.98	8	3.56	8	6.15	8	8.74	8	11.34
1.0040	1.03	1.0140	3.62	1.0240	6.20	1.0340	8.79	1.0440	11.39
2	1.08	2	3.67	2	6.25	2	8.85	2	11.44
4	1.13	4	3.72	4	6.31	4	8.90	4	11.49
6	1.18	6	3.77	6	6.36	6	8.95	6	11.55
8	1.24	8	3.82	8	6.41	8	9.00	8	11.60
1.0050	1.29	1.0150	3.87	1.0250	6.46	1.0350	9.05	1.0450	11.65
2	1.34	2	3.93	2	6.51	2	9.10	2	11.70
4	1.39	4	3.98	4	6.56	4	9.16	4	11.75
6	1.45	6	4.03	6	6.62	6	9.21	6	11.81
8	1.50	8	4.08	8	6.67	8	9.26	8	11.86
1.0060	1.55	1.0160	4.13	1.0260	6.72	1.0360	9.31	1.0460	11.91
2	1.60	2	4.19	2	6.77	2	9.36	2	11.96
4	1.65	4	4.24	4	6.82	4	9.42	4	12.01
6	1.70	6	4.29	6	6.88	6	9.47	6	12.06
8	1.76	8	4.34	8	6.93	8	9.52	8	12.12
1.0070	1.81	1.0170	4.39	1.0270	6.98	1.0370	9.57	1.0470	12.17
2	1.86	2	4.44	2	7.03	2	9.62	2	12.22
4	1.91	4	4.50	4	7.08	4	9.68	4	12.27
6	1.96	6	4.55	6	7.13	6	9.73	6	12.32
8	2.01	8	4.60	8	7.19	8	9.78	8	12.38
1.0080	2.07	1.0180	4.65	1.0280	7.24	1.0380	9.83	1.0480	12.43
2	2.12	2	4.70	2	7.29	2	9.88	2	12.48
4	2.17	4	4.75	4	7.34	4	9.93	4	12.53
6	2.22	6	4.81	6	7.39	6	9.99	6	12.58
8	2.27	8	4.86	8	7.45	8	10.04	8	12.64
1.0090	2.32	1.0190	4.91	1.0290	7.50	1.0390	10.09	1.0490	12.69
2	2.38	2	4.96	2	7.55	2	10.14	2	12.74
4	2.43	4	5.01	4	7.60	4	10.19	4	12.79
6	2.48	6	5.06	6	7.65	6	10.25	6	12.84
8	2.53	8	5.11	8	7.70	8	10.30	8	12.90

Table 60.

Table for the Determination of E—*continued*.

x.	E.	x.	E.	x.	E.	x.	E.	x.	E.
1.0500	12.95	1.0610	15.81	1.0720	18.69	1.0830	21.57	1.0940	24.46
2	13.00	2	15.87	2	18.74	2	21.62	2	24.51
4	13.05	4	15.92	4	18.79	4	21.67	4	24.57
6	13.10	6	15.97	6	18.84	6	21.73	6	24.62
8	13.15	8	16.02	8	18.90	8	21.78	8	24.67
1.0510	13.21	1.0620	16.07	1.0730	18.95	1.0840	21.83	1.0950	24.72
2	13.26	2	16.13	2	19.00	2	21.88	2	24.78
4	13.31	4	16.18	4	19.05	4	21.94	4	24.82
6	13.36	6	16.23	6	19.10	6	21.99	6	24.88
8	13.42	8	16.28	8	19.16	8	22.04	8	24.93
1.0520	13.47	1.0630	16.33	1.0740	19.21	1.0850	22.09	1.0960	24.99
2	13.52	2	16.39	2	19.26	2	22.15	2	25.04
4	13.57	4	16.44	4	19.31	4	22.20	4	25.09
6	13.62	6	16.49	6	19.37	6	22.25	6	25.14
8	13.68	8	16.54	8	19.42	8	22.30	8	25.20
1.0530	13.73	1.0640	16.60	1.0750	19.47	1.0860	22.36	1.0970	25.25
2	13.78	2	16.65	2	19.52	2	22.41	2	25.30
4	13.83	4	16.70	4	19.58	4	22.46	4	25.36
6	13.89	6	16.75	6	19.63	6	22.51	6	25.41
8	13.94	8	16.80	8	19.68	8	22.57	8	25.46
1.0540	13.99	1.0650	16.86	1.0760	19.73	1.0870	22.62	1.0980	25.51
2	14.04	2	16.91	2	19.79	2	22.67	2	25.56
4	14.09	4	16.96	4	19.84	4	22.72	4	25.62
6	14.14	6	17.01	6	19.89	6	22.78	6	25.67
8	14.20	8	17.07	8	19.94	8	22.83	8	25.72
1.0550	14.25	1.0660	17.12	1.0770	20.00	1.0880	22.88	1.0990	25.78
2	14.30	2	17.17	2	20.05	2	22.93	2	25.83
4	14.35	4	17.22	4	20.10	4	22.99	4	25.88
6	14.41	6	17.27	6	20.15	6	23.04	6	25.93
8	14.46	8	17.33	8	20.20	8	23.09	8	25.99
1.0560	14.51	1.0670	17.38	1.0780	20.26	1.0890	23.14	1.1000	26.04
2	14.56	2	17.43	2	20.31	2	23.20	2	26.09
4	14.61	4	17.48	4	20.36	4	23.25	4	26.14
6	14.67	6	17.54	6	20.41	6	23.30	6	26.20
8	14.72	8	17.59	8	20.47	8	23.35	8	26.25
1.0570	14.77	1.0680	17.64	1.0790	20.52	1.0900	23.41	1.1010	26.30
2	14.82	2	17.69	2	20.57	2	23.46	2	26.35
4	14.87	4	17.75	4	20.62	4	23.51	4	26.41
6	14.93	6	17.80	6	20.68	6	23.57	6	26.46
8	14.98	8	17.85	8	20.73	8	23.62	8	26.51
1.0580	15.03	1.0690	17.90	1.0800	20.78	1.0910	23.67	1.1020	26.56
2	15.08	2	17.95	2	20.83	2	23.72	2	26.62
4	15.14	4	18.01	4	20.89	4	23.77	4	26.67
6	15.19	6	18.06	6	20.94	6	23.83	6	26.72
8	15.24	8	18.11	8	20.99	8	23.88	8	26.78
1.0590	15.29	1.0700	18.16	1.0810	21.04	1.0920	23.93	1.1030	26.83
2	15.35	2	18.22	2	21.10	2	23.99	2	26.88
4	15.40	4	18.27	4	21.15	4	24.04	4	26.93
6	15.45	6	18.32	6	21.20	6	24.09	6	26.99
8	15.50	8	18.37	8	21.25	8	24.14	8	27.04
1.0600	15.55	1.0710	18.43	1.0820	21.31	1.0930	24.20	1.1040	27.09
2	15.61	2	18.48	2	21.36	2	24.25	2	27.15
4	15.66	4	18.53	4	21.41	4	24.30	4	27.20
6	15.71	6	18.58	6	21.46	6	24.35	6	27.25
8	15.76	8	18.63	8	21.52	8	24.41	8	27.30

Table 60.

Table for the Determination of E—*continued*.

x.	E.	x.	E.	x.	E.	x.	E.	x.	E.
1.1050	27.35	1.1070	27.88	1.1090	28.41	1.1110	28.94	1.1130	29.47
2	27.41	2	27.93	2	28.46	2	28.99	2	29.52
4	27.46	4	27.99	4	28.51	4	29.04	4	29.57
6	27.51	6	28.04	6	28.57	6	29.09	6	29.62
8	27.57	8	28.09	8	28.62	8	29.15	8	29.68
1.1060	27.62	1.1080	28.15	1.1100	28.67	1.1120	29.20	1.1140	29.73
2	27.67	2	28.20	2	28.73	2	29.25	2	29.78
4	27.72	4	28.25	4	28.78	4	29.31	4	29.83
6	27.78	6	28.30	6	28.83	6	29.36	6	29.89
8	27.83	8	28.36	8	28.88	8	29.41	8	29.94
								1.1150	29.99

(a) If E is not greater than 3, the final determination of the extract is effected as follows:—A weighed platinum basin about 85 mm. in diameter, 20 mm. in depth, holding 75 c.c., and weighing about 20 g., is placed on a rapidly boiling water-bath, and 50 c.c. of wine at 15° are allowed to flow into it. As soon as the sample reaches a syrupy consistency, the dish and residue are placed in a drying cupboard, in the jacket of which water is rapidly boiling, and after drying thus for two and a half hours, it is placed in a desiccator to cool, and the amount of extract found by weighing.

(b) If E is more than 3, but less than 4, a quantity such that not more than 1.5 g. of extract will be left is measured out into the platinum dish, and the process completed as under (a).

(c) If E is 4 or more, this number finally gives the weight in grams of extract in 100 c.c. of wine.

To give an opinion on a wine which, by its description, purports to come from a vine-growing district in Germany, and similarly to find the amount of extract of the completely fermented wine on the same basis, use is made of the data obtained in the estimation of sugar (*cf.* No. 10, p. 767). If the sugar is more than 0.1 g. per 100 c.c. of wine, the quantity in excess must be deducted from the extract found under No. 3 (a), 3 (b), or 3 (c). The result represents the extract of the completely fermented wine.

Note.—In the estimation of the extract, wines with less than 4 g. of extract per 100 c.c. are subjected to a fundamentally different treatment from those with 4 g. or more per 100 c.c. Those with less than 4 g. per

100 c.c. are evaporated and the extract weighed; in the case of those with more, the extract is determined indirectly from the specific gravity of the wine after the removal of the alcohol, and making up to the original volume. It is therefore necessary first to determine which method is to be applied to a given sample. This is done by calculation, with the help of the formula given above. The value of x determined by this formula gives the specific gravity of the de-alcoholised and made-up wine. The value of E corresponding to x gives the number of grams of extract in 100 c.c. of wine corresponding to the specific gravity x .

The exact determination of the extract is impossible in the strict sense, on account of the volatility of the glycerol and the possible decomposition which occurs on heating the extract. The methods prescribed must therefore be strictly followed if comparable results are to be obtained. Even then differences may occur in the results obtained which are important, especially in the case of wines with a low proportion of extract. For this reason the Commission charged with preparing statistics of the German wine industry has, on the suggestion of W. Möslinger,¹ published the following data for the direct determination of the extract.

50 c.c. of wine, measured at 15°, are evaporated to a syrupy consistency in a platinum dish 85 mm. in diameter at its rim, 20 mm. deep, of 75 c.c. capacity and weighing about 20 g., on a rapidly boiling water-bath provided with a ring or opening 60 mm. in diameter, in a place free from draughts. This operation requires about forty minutes. Towards the end of this time the progress of the evaporation is watched continuously, and as soon as the wine flows with difficulty all parts of the contents of the dish are continually moistened, as far as possible, with the portion remaining fluid, by frequent inclination of the dish in all directions, until the evaporation is completed. This stage is reached as soon as the liquid cannot immediately, but only after a short interval, be united into a slowly flowing drop, and becomes almost immobile on cooling. The dish is then dried on the outside and transferred to the interior of a specially arranged drying oven² containing boiling water. After two and a half hours' heating, during which period the water-level must remain constant and the cupboard on no account be opened, the dish is covered as quickly as possible with its cover, or a glass or mica plate, taken out, and weighed immediately after cooling in a desiccator.

According to experiments by C. Amthor,³ the height of the barometer, and consequently the height above sea-level of the locality, exert

¹ *Forschungsberichte über Lebensmittel*, 1896, 3, 286.

² The construction of the drying oven is fully described in the original paper. (*Loc. cit.*)

³ *Z. Unters. Nahr. u. Genussm.*, 1898, 1, 812.

an appreciable influence on the result of the extract determination, in so far as the boiling point of the water and in consequence the temperature at which the extract is dried, are dependent upon these factors.

The official extract Table is really a cane sugar Table, since the relation between the specific gravity and extract of de-alcoholised sweet wines is not exactly known, and cane sugar solutions have a specific gravity approximately equal to that of the aqueous solutions of sweet wine extracts.

A. Halenke and W. Möslinger¹ have calculated an extract Table for wine analysis at 15°, based on the results of evaporating musts; W. Fresenius has extended this table by extrapolation down to the specific gravity of 1.0000.²

4. Estimation of Mineral Constituents.

If the wine contains less than 4 g. of extract per 100 c.c., the extract obtained as in 3 (a) or 3 (b) is carefully carbonised by moving a small flame backwards and forwards beneath the platinum dish. The carbon is then broken up with a thick platinum wire, repeatedly washed with hot water, and the aqueous extract filtered through a small filter of known ash into a small beaker. After the carbon has been completely extracted, the filter is dried in the platinum basin with the carbon, and both completely incinerated. When the ash has become white the filtered solution is poured back into the dish and evaporated to dryness, the residue moistened with ammonium carbonate solution, very gently ignited, allowed to cool in a desiccator, and weighed.

If the wine contains 4 g. or more extract per 100 c.c., 25 c.c. of the wine are evaporated in a good-sized platinum basin and the residue very carefully ignited; the resulting vesicular carbon is further treated in the manner described above.

Note.—The moistening with ammonium carbonate solution is unnecessary, and sometimes even disadvantageous. The hygroscopic nature of the ash renders it necessary to cover the dish during weighing.

Wines very rich in sugar can be incinerated only with great difficulty, as the melting extract becomes puffed up and easily froths over even in a large dish. In such cases, 50 c.c. of the wine may be deprived of its alcohol, diluted to a sugar-content of 10-15 per cent., sown with a trace of yeast, and fermented at 25°-30°. The fermented liquid may then be washed, along with its sediment, into a platinum basin, evaporated, and the residue incinerated as described.

¹ *Z. anal. Chem.*, 1897, 36, 413.

² Borgmann's *Anleitung zur. chem. Untersuchung des Weines*, W. Fresenius, 2nd ed., 1898, p. 208.

5. Estimation of the Sulphuric Acid in Red Wines.

The sulphuric acid is precipitated with barium chloride solution in 50 c.c. of wine, previously heated and rendered acid with hydrochloric acid.

With red wines the barium sulphate precipitate is always coloured red, as other substances are precipitated simultaneously with it. Such precipitates are ignited, fused with sodium carbonate and potassium nitrate, the melt dissolved in water, filtered, well washed, the liquid acidulated with hydrochloric acid, the nitric acid driven off by evaporation, and the sulphuric acid precipitated hot with barium chloride.

6. Estimation of the Free Acids (Total Acids).

25 c.c. of the wine are heated until boiling begins, and the hot liquid titrated with a standard alkali solution of not less than $N/4$ strength. If a normal solution is used burettes of about 10 c.c. volume, allowing $\frac{1}{100}$ c.c. to be estimated, must be employed. The end-point is found by spotting on sensitive violet litmus paper; this point is reached when a drop placed on the dry litmus paper causes no further reddening. The free acids are calculated as tartaric acid.

Note.—Halenke and Möslinger¹ recommended, instead of litmus paper, the use of a paper prepared with azolitmic acid, a constituent of the colouring matter of litmus. Another proposal of Halenke and Möslinger is the standardisation of the standard alkali used for determining the total acid against pure tartaric acid, powdered and dried over sulphuric acid.

7. Estimation of the Volatile Acids.

The volatile acids are distilled off with steam. From 50 c.c. of wine, 25 c.c. are distilled off in a current of steam; the flask is warmed in such a manner that the volume of its contents is not further altered. The maintenance of the volume at 25 c.c. is of importance to the result. The distillation is stopped when 200 c.c. have come over. Phenolphthalein is added to the distillate, which is then titrated. The volatile acids are calculated as acetic acid.

Note.—According to W. Möslinger² the diameter of the steam jet opening should be 1 mm. and the internal diameter of the steam tube 4 mm. The burners must be so regulated that the 200 c.c. of distillate are obtained in thirty to forty-five minutes.

It is only in the case of very sour wines containing much acetic acid that the total quantity of acetic acid is not found in the first 200 c.c.

¹ *Z. anal. Chem.*, 1895, 34, 274.

² *Forschungsberichte über Lebensmittel*, 1897, 4, 329.

If the distillation is continued beyond this point, small quantities of acid always come over; in sound wines they consist chiefly of lactic acid.

8. Estimation of Non-Volatile Acids.

The quantity of non-volatile acids in a wine to be returned as tartaric acid, is found by calculation as follows:—

If a is the number of grams of free acid, calculated as tartaric acid, in 100 c.c. wine,

b the number of grams of volatile acids in 100 c.c. of wine, calculated as acetic acid,

x the number of grams of non-volatile acids in 100 c.c. of wine, calculated as tartaric acid,

then $x = (a - 1.25 b)$ grams of non-volatile acids, calculated as tartaric acid, in 100 c.c. wine.

9. Estimation of the Glycerol.

(a) *In Wines with less than 2 g. of Sugar per 100 c.c.*

For this estimation 100 c.c. of wine are evaporated in a porcelain basin on the water-bath to 10 c.c., 1 g. of quartz sand added to the residue, followed by sufficient milk of lime containing 40 per cent. of calcium hydroxide, to give 1.5-2 c.c. of milk of lime to every 1 g. of extract, and the whole evaporated to dryness. To the moist residue is added about 5 c.c. of alcohol of 96 per cent. by volume, the mass adhering to the walls of the dish loosened with a spatula, and rubbed up to a paste with 96 per cent. alcohol, by means of a small pestle; the spatula and pestle are carefully washed with the alcohol. The dish is then heated on the water-bath with continuous stirring until boiling begins, when the turbid alcoholic liquid is poured through a small funnel into a 100 c.c. flask. The powdered residue remaining in the dish is extracted hot, with stirring, with a further quantity of alcohol of 96 per cent. by volume, the extract poured into the 100 c.c. flask, and the process repeated until the quantity of extract amounts to about 95 c.c. The insoluble residue remains in the dish. The small funnel in the neck of the flask is then rinsed down with alcohol, the alcohol extract cooled to 15°, and made up to 100 c.c. with 96 per cent. alcohol. After vigorous shaking, the alcoholic extract is filtered through a pleated filter into a graduated cylinder, 90 c.c. of it transferred to a porcelain dish, and evaporated on the water-bath, violent boiling of the alcohol being avoided. The residue is taken up with a small quantity of absolute alcohol, the solution poured into a graduated stoppered

cylinder, and the dish washed with a small quantity of absolute alcohol until the solution measures exactly 15 c.c. To this solution are added three successive portions of 7.5 c.c. of absolute ether, and the liquid vigorously shaken after each addition. The cylinder is stoppered, and allowed to stand until the liquid has become quite clear, when it is transferred to a stoppered weighing-bottle. After the filter and the glass cylinder have been washed out with about 5 c.c. of a mixture of 1 vol. of absolute alcohol and $1\frac{1}{2}$ vols. of absolute ether, and the washings transferred to the weighing-bottle the alcohol-ether solution is heated on a hot, but not boiling, water-bath, violent boiling being avoided. When the residue in the weighing-bottle has become viscous, it is placed for one hour in a drying oven, surrounded by vigorously boiling water, then allowed to cool in a desiccator, and weighed.

Calculation.—If a grams of glycerol are weighed, then 100 c.c. of the wine contain $a \times 1.111$ g. of glycerol.

(b) *In Wines with 2 g. or more Sugar in 100 c.c.*

In this case 50 c.c. of wine are heated in a roomy flask on the water-bath, and 1 g. of quartz sand, followed by successive small quantities of milk of lime, added until the mixture, which at first becomes darker, acquires a lighter colour and an alkaline smell. The mixture is then heated on the water-bath with constant shaking. After cooling, 100 c.c. of alcohol of 96 per cent. by volume are added, the precipitate which forms allowed to settle, the alcoholic solution filtered off, and the precipitate washed with 96 per cent. alcohol. The filtrate is concentrated, and further treated as described above.

Calculation.—If a grams of glycerol are weighed, then 100 c.c. of the wine contain $a \times 2.222$ g. of glycerol.

If the result of the sugar estimation is not given, it must always be stated whether the glycerol was determined as in 9 (a) or 9 (b).

Note.—This method of estimating glycerol is very faulty. On the one hand, losses of glycerol on evaporation are inevitable, and on the other hand, substances other than glycerol are included in the ether-alcohol extract; this is especially the case with wines rich in sugar. Several other methods of estimating glycerol have been proposed.¹

10. Estimation of the Sugar.

The estimation of the sugar is effected gravimetrically by means of Fehling's solution.

¹ Cf. K. Windisch, *Chemische Untersuchung und Beurteilung des Weines*, p. 80; also, S. Zeisel and R. Fanto, *Zeitschr. f. Landw. Versuchswesen Österreich*, 1902, 5, 729; *Z. anal. Chem.*, 1903, 42, 549; M. Stritar, *Z. anal. Chem.*, 1903, 42, 579; J. Schuch, *Zeitschr. f. Landw. Versuchswesen Österreich*, 1904, 7, 111.

Preparation of the Solutions required.

1. *Copper Sulphate Solution.*—69.278 g. of crystallised copper sulphate are dissolved in water and made up to 1 litre.

2. *Alkaline Rochelle Salt Solution.*—346 g. of Rochelle salt (potassium sodium tartrate) and 103.2 g. of sodium hydroxide are dissolved in water, made up to 1 litre, and filtered through asbestos.

The two solutions must be stored separately.

Preparation of the Wine for the Sugar Estimation.

The approximate sugar-content of the wine is first determined by subtracting 2 from the amount of extract. Wines thus shown to contain not more than 1 g. of sugar in 100 c.c. may be used undiluted for the sugar determination; those containing more must be diluted until they contain at most 1 g. of sugar per 100 c.c. The figure found for the approximate sugar-content (extract minus 2) shows how many times the wine must be diluted to give a solution containing not more than 1 per cent. of sugar. To simplify measurement and calculation the figure (extract minus 2) is taken as the next higher whole number. The quantity of wine taken is such that the volume, after dilution, is at least 100 c.c.

Method of Estimation of the Sugar in Wine.

For this purpose 100 c.c. of the wine, or, in the case of a wine containing more than 1 per cent. of sugar, 100 c.c. of wine diluted as described above, are measured off in a measuring flask, neutralised with alkali in a porcelain dish, and evaporated to 25 c.c. on the water-bath. To remove tannin and colouring matter, in the case of a red wine or of a white wine containing much tannin, from 5-10 g. of purified animal charcoal are added to the de-alcoholised wine residue, the mixture stirred well on the water-bath with a glass rod, and the liquid filtered back into the 100 c.c. flask. The animal charcoal is washed out carefully with hot water until the filtrate amounts to nearly 100 c.c. after cooling; 3 drops of a saturated sodium carbonate solution are then added, the liquid shaken and made up to 100 c.c. at 15°. If the addition of sodium carbonate causes a turbidity the mixture is allowed to stand for two hours and is then filtered. The sugar is estimated in the filtrate.

To remove the tannin and colouring matter, lead acetate may be used instead of animal charcoal. The method in that case is as follows:—160 c.c. of wine are neutralised as described, the alcohol removed, and the residue made up with water at 15° to the original volume; 16 c.c. of lead acetate solution are added, the liquid shaken and filtered, 8 c.c. of saturated sodium carbonate solution or of sodium sulphate solution saturated at 20° added to 88 c.c. of the filtrate, the

liquid shaken and filtered, and the sugar determined in the filtrate. The volume of the wine is increased one-fifth by the addition of the lead acetate and sodium carbonate solutions, and this must be taken account of in the calculation of the content of sugar.

(a) *Estimation of the Invert Sugar.*

A mixture of 25 c.c. of copper sulphate solution, 25 c.c. of Rochelle salt solution, and 25 c.c. of water is heated to boiling upon a wire gauze in a perfectly smooth porcelain basin. Into the boiling mixture 25 c.c. of the wine, prepared as described, are allowed to flow from a pipette, and boiling continued for exactly two minutes from the moment at which the interrupted ebullition again reaches its full vigour. The separated cuprous oxide is immediately filtered off by means of the pump on to an asbestos filter-tube, and washed out first with water and then with alcohol and ether. After drying at 100° , the tube containing the cuprous oxide is first heated strongly with access of air. It is then connected with a hydrogen-generating apparatus, the copper oxide formed heated with a small flame and reduced completely to metallic copper, which is allowed to cool in a current of hydrogen, and then weighed. The quantity of invert sugar corresponding to the amount of copper weighed is obtained by means of a Table such as that given in the section on "Sugar," this Vol., p. 557.

The asbestos filter-tube is cleaned by dissolving the copper in hot nitric acid, washing out with water, alcohol and ether, drying, and heating in a current of hydrogen.

(b) *Estimation of the Cane Sugar.*

50 c.c. of the sample treated as described, de-alcoholised, rendered alkaline, and freed from colouring matter and tannin if necessary, are measured with a pipette into a flask of about 100 c.c. capacity, exactly neutralised with hydrochloric acid, 5 c.c. of a 1 per cent. solution of hydrochloric acid added, and the mixture heated for thirty minutes on a boiling water-bath. The liquid is then exactly neutralised, rendered slightly alkaline with sodium carbonate solution, and filtered through a small filter into a 50 c.c. flask, which is filled to the mark with the rinsings. The sugar is then determined as described above, in 25 c.c. of the solution thus obtained.

Calculation.—The quantity of copper obtained after inversion with hydrochloric acid is calculated into grams of invert sugar per 100 c.c. wine as follows:—

If a is the number of grams of invert sugar in 100 c.c. of wine found before inversion with hydrochloric acid,

b the number of grams of invert sugar in 100 c.c. of wine after inversion with hydrochloric acid,
 then $x = 0.95 (b-a)$ grams of cane sugar in 100 c.c. of the wine.

It must always be stated whether tannin and colouring matter were removed by animal charcoal or by lead acetate.

Notes.—1. Sweet wines very rich in sugar cannot be measured off for dilution, as they adhere to the walls of the burette. Such wines are weighed, and the volume calculated by the formula:—

$$V = \frac{1.00228 \times p}{d},$$

in which V is the volume, p the weight, and d the specific gravity of the wine.

2. The efficiency of the animal charcoal depends very much upon its condition. To purify commercial animal charcoal it is finely powdered, strongly ignited, extracted with hydrochloric acid, and then washed with water until all acid is removed. The purified animal charcoal is kept under water.

3. The use of lead acetate is usually more convenient than that of animal charcoal. The removal of the excess by means of sodium phosphate or sodium oxalate is also recommended.

4. Since very few wines contain cane sugar, the estimation of the reducing sugar can often be considerably simplified by omitting the neutralisation and concentration of the wine and treating the original wine with lead acetate, as in the determination of the rotatory power (p. 771).

5. Instead of reducing the cuprous oxide, or the cupric oxide obtained from it by oxidation, and weighing the metallic copper, it has been proposed to weigh the copper oxide; this proposal deserves consideration, as it means a material simplification of the process, and comparative experiments have shown a satisfactory agreement between the sugar values from the metallic copper and those from copper oxide.

6. According to P. Kulisch,¹ the addition of 5 c.c. of 1 per cent. hydrochloric acid does not suffice for the complete inversion of wines which have not been diluted before the sugar estimation, since the acid reacts with the alkali salts of the organic acids in the wine, and the organic acids set free have much less inverting effect than the hydrochloric acid. The prescribed quantity of hydrochloric acid only suffices for wines which have been diluted to at least five times their original volume. Kulisch recommends the use of 0.5-1 c.c. of 25 per cent. hydrochloric acid for wines which have not been diluted. If such quantities of hydrochloric acid are used the amount of sugar found

¹ *Z. angew. Chem.*, 1897, 10, 45, 205.

is often too large: an increase in the sugar by inversion of less than 0.03 per cent. in the case of ordinary wines and of 0.2 per cent. for sweet wines may be neglected. It is better to use oxalic acid for inversion, 1 g. of crystallised oxalic acid per 50 c.c. of wine for wines diluted to twice their volume or more, and 2 g. for other wines. W. Möslinger¹ has suggested warming 75 c.c. of sweet wines with 1.5 g. of oxalic acid for twenty minutes at 70°.

The reducing sugar can also be determined volumetrically either with Fehling's solution or by the method of Sachsse, with alkaline potassium mercury iodide solution.² The former of these methods is fully described in the section on "Sugar," this Vol., p. 563. An alternative method for the estimation of reducing sugars has also been given by J. Kjeldahl.³

11. The Rotatory Power (Polarisation).

For the determination of the behaviour of wine to polarised light, large, accurate instruments must be used, giving readings to $\frac{1}{10}$ degree. The result is to be given in degrees, on a layer 200 mm. long of the original wine, and the rotation is to be measured at 15°.

Method of determining the Polarisation of Wines.

(a) *White Wines*.—In the case of white wines, contained in a measuring cylinder, 3 c.c. of lead acetate solution are added to 60 c.c., and the resulting precipitate filtered off. To 31.5 c.c. of the filtrate are added 1.5 c.c. of a saturated solution of sodium carbonate, the resulting precipitate filtered off, and the polarisation of the filtrate determined. The volume of the wine is thereby increased by $\frac{1}{10}$, and this must be taken into consideration.

(b) *Red Wines*.—In this case 60 c.c. of the wine are neutralised with alkali, evaporated to $\frac{1}{3}$ of the original volume on the water-bath, filtered, made up to the original volume, and 6 c.c. of lead acetate solution added. The precipitate is filtered off, 3 c.c. of saturated sodium carbonate solution added to 33 c.c. of the filtrate, the precipitate removed by filtration, and the rotation of the filtrate determined. The volume of the red wine is increased $\frac{1}{5}$ by the addition of the reagents.

If the decolorisation of a wine is not complete with lead acetate, resort is had to animal charcoal. By means of a graduated flask 50 c.c. of wine are measured into a porcelain dish, exactly neutralised with alkali, and the neutralised wine evaporated to about 25 c.c. To the wine thus deprived of alcohol are added 5-10 g. of purified animal charcoal, the mixture heated on the water-bath, well stirred with a

¹ *Chem. Zeit.*, 1897, 21, 637.

² *Z. anal. Chem.*, 1877, 16, 121; 1881, 20, 447.

³ *Ibid.*, 1896, 35, 444, 646.

glass rod, and the liquid filtered off. The animal charcoal is washed carefully with hot water until the filtrate amounts to 75-100 c.c., according to the quantity of sugar in the sample. The filtrate is then evaporated down to 30-40 c.c. in a porcelain dish on the water-bath, the residue filtered into the 50 c.c. graduated flask, the porcelain dish and filter washed with water, and the filtrate made up to the mark. The rotation of the filtrate is then determined; there is no dilution of the wine by this method of preparation.

Note.—According to C. Amthor,¹ it is not a matter of indifference whether the wine is decolorised with lead acetate, or with animal charcoal. Wines which have been treated with animal charcoal show a feeble dextro-rotation, in consequence of their containing gum or similar substances, while they are often slightly lævo-rotatory after treatment with lead acetate, which precipitates these substances. Lead acetate is generally to be preferred to animal charcoal, as being more convenient to use; sometimes, however, strongly coloured red wines cannot be completely decolorised by it.

12. Detection of Impure Glucose by Polarisation.

(a) If, at most, 0.1 g. of reducing sugar in 100 c.c. wine has been found by No. 10, and the wine, as determined by No. 11, is either lævo-rotatory, or has no dextro-rotation, or at most $+0^{\circ}.3$, no impure glucose has been added to the wine.

(b) If, in the estimation of sugar by No. 10, at most 0.1 g. of reducing sugar has been found, and the wine has a dextro-rotation of more than $0^{\circ}.3$, and at most $0^{\circ}.6$, the wine may possibly contain dextrin; this is then to be tested for by No. 19 (p. 782). In addition, the unfermented constituents of impure glucose should be looked for by the method described in 12 (d).

(c) If in the estimation of sugar by No. 10 at most 0.1 g. of total sugar in 100 c.c. of wine has been found, and the wine shows a dextro-rotation of more than $0^{\circ}.6$, dextrin must be looked for immediately by No. 19. If present, the detection of the unfermented constituents of the impure glucose is proceeded with by the method described in No. 12 (d). If dextrin is not present, the wine contains the unfermented constituents of impure glucose.

(d) If in the estimation of sugar by No. 10 more than 0.1 g. of total sugar was found in 100 c.c. of wine, the addition of impure glucose is detected as follows:—

(a) 210 c.c. of the wine are evaporated to one-third of this volume on the water-bath, made up with water to the original volume, placed in a flask, 5 g. of active brewer's yeast free from optically active

¹ *Z. Unters. Nahr. u. Genussm.*, 1898, 2, 814.

constituents added, and the whole allowed to stand at 20°-25° until fermentation is complete.

(β) A few drops of a 20 per cent. potassium acetate solution are added to the completely fermented liquid, and the whole evaporated in a porcelain dish on the water-bath, with the addition of quartz sand, until a thin syrup is obtained; 200 c.c. of alcohol of 90 per cent. by volume are then added gradually to the residue, with continuous stirring. After the liquid has become clear, the alcoholic extract is filtered into a flask, the residue and filter washed with a small quantity of alcohol of 90 per cent. by volume, and most of the alcohol distilled off. The rest of the alcohol is evaporated off, and the residue made up to about 10 c.c. with water. A paste of 2-3 g. of purified animal charcoal in water is added, and well stirred in, the decolorised liquid filtered into a small graduated cylinder, and the animal charcoal washed out hot with water, until the filtrate, cooled to 15°, measures 30 c.c. If it shows a rotation of more than +0°·5, the wine contains the unfermented constituents of impure glucose. If the rotation is exactly +0°·5, or only slightly above or below this figure, the animal charcoal is further extracted with hot water, until the filtrate from it measures 30 c.c. The rotation observed for this filtrate is added to that for the first. If the second rotation is more than one-fifth of the first, the charcoal must be washed with 30 c.c. of hot water a third time, and the rotation of the filtrate determined.

The dextro-rotation may also be caused by certain constituents of many kinds of honey.

Note.—In the case of ordinary wines the determination of the rotation can be carried out at the ordinary temperatures; in other cases the observation tube is enclosed in a cooling jacket.

L. Grünhut¹ has shown that fermentation is not always necessary to prove the presence of impure glucose in a wine showing more than 0·1 g. reducing sugar in a 100 c.c. If the specific rotation $[\alpha]_D$ of the total reducing sugar in the wine is calculated by the formula:—

$$[\alpha]_D = \frac{100\alpha}{2(c-0\cdot1)},$$

in which α is the angle of rotation in the 200 mm. tube, and c the number of grams of sugar in 100 c.c. of wine, the presence of impure glucose (and of cane sugar) is impossible if $[\alpha]_D$ is negative, and greater than -45°; it is only when $[\alpha]_D$ is positive, or lies between 0° and -45°, that it is necessary to ferment the sugar. This is best carried out with pure culture yeast, when this is to be had; considerably less than 5 g. of this suffices. Pressed yeast must not be used, as it

¹ *Z. anal. Chem.*, 1897, 36, 168.

partly ferments those portions of the impure glucose which are fermented with difficulty.

F. Wirthle¹ has shown that wines with less than 0.1 g. of sugar per 100 c.c., and a rotation of less than $+0.^\circ 3$ may still contain impure glucose.

13. Detection of Foreign Colouring Matter in Red Wines.

Red wines should always be tested for coal tar colours, and for their behaviour to lead acetate. For this purpose a woollen thread, mordanted with alum and sodium acetate, is boiled in the wine, and the behaviour of the dye on the woollen thread examined towards reagents. The method used for detecting the individual foreign colouring matters must always be given.

Note.—The following methods may be used for the detection of foreign dyes in red wines :—

(a) *Detection of Coal-Tar Colours in Red Wines.*²

(a) *The Wool Test (N. Arata*³).—Three or four threads of white wool mordanted with alum and sodium acetate are boiled for ten minutes in a porcelain dish or a beaker with 50-100 c.c. of the red wine and 5-10 c.c. of 10 per cent. potassium sulphate solution; the wool is then removed and washed with water. If the wine contains a coal-tar colour, the wool is coloured more or less red; unadulterated wines colour the wool faintly red. The washed wool is treated with ammonia. If the wine was coloured with a coal-tar colour, the wool either remains red, or becomes yellowish, which goes back to red when the ammonia is washed out; in absence of tar colours the faint red colour of the wool is converted by the ammonia into a dirty greenish-white.

(β) *Preliminary Test with Lead Acetate.*—A mixture of 20 c.c. of the red wine and 10 c.c. of lead acetate solution is gently warmed, shaken, and filtered. A red filtrate points to the presence of coal-tar colours, but it is to be borne in mind that very deep-coloured southern wines may give a coloured filtrate. The red filtrate may be subjected to treatment with amyl alcohol (see (δ)).

(γ) *Extraction of the Wine with Ether after the Addition of an Excess of Ammonia.*—After the addition of 5 c.c. of ammonia to 100 c.c. of the wine, it is shaken out with 30 c.c. of ether. Of the clear ethereal layer 20 c.c. are removed by means of a pipette and the ether evaporated off in a porcelain dish in which is placed a white woollen

¹ *Chem. Zeit.*, 1903, **27**, 246.

² Cf. A. Hasterlik, *Mitteil. a. d. Pharm. Institute u. Labor. f. angew. Chemie der Universität Erlangen*, 1889, Part II., p. 51; also K. Windisch, *Die Chemische Untersuchung und Beurteilung des Weines*, pp. 155-162.

³ *Z. anal. Chem.*, 1889, **28**, 639.

thread 5 cm. long. If this is coloured red, after removal of the ether, the wine contains coal-tar colouring matter.

(δ) *Extraction of the Wine with Amyl Alcohol after the Addition of an Excess of Ammonia*.—An excess of ammonia is added to 100 c.c. of the wine and the mixture extracted with amyl alcohol. If the extract is red, coal-tar colours are present.

(ε) *The Mercuric Oxide Test (Cazeneuve¹)*.—10 c.c. of the wine are shaken in the cold with 0.2 g. of yellow mercuric oxide for one minute; when the mercuric oxide has settled, the liquid is filtered off through a three- or four-fold moistened filter. A further quantity of 10 c.c. of wine is boiled up once with 0.2 g. of yellow mercuric oxide and shaken for a minute; after complete settling of the mercuric oxide the liquid is filtered through a three- or four-fold moistened filter. If the filtrate is turbid and grey, the shaking or boiling was too short, or the mercuric oxide insufficiently settled, and the test is repeated. A clear, coloured filtrate shows the presence of coal-tar colours. If the filtrate is colourless, dyes may nevertheless be present in the wine, for some coal-tar colours, like the red colouring matter of wine and other vegetable colouring matter, are retained by mercuric oxide.

G. Comboni² states that in the case of the deep-coloured southern red wines 2-3 g. of freshly precipitated mercuric oxide must be used for 10 c.c. of wine, to decolorise it completely. Wines from American vines are not decolorised at all by mercuric oxide.

(b) *Detection of added Vegetable Colouring Matter in Red Wines.*

Of vegetable colours only that of the ink-berry (*Phytolacca decandra*) can be recognised with some certainty; methods for detecting others (bilberry, elderberry, etc.) are very uncertain.

For testing wines for the dye of the ink-berry the following two methods may be used:—

(1) *Detection of the Ink-berry Dye with Lead Acetate*.—To 20 c.c. of the wine are added 5 c.c. of lead acetate solution; if the dye of ink-berry is present a characteristic violet-red precipitate is formed.

(2) *Detection of the Ink-berry Dye with Alum and Sodium Carbonate (J. Macagno³ and R. Heise⁴)*.—To 20 c.c. of the wine are added 10 c.c. of a 10 per cent. potash alum solution and then sufficient 10 per cent. sodium carbonate solution to render the solution neutral, or at most slightly alkaline, and in any case not acid; about 10 c.c. of the sodium carbonate solution are necessary for this purpose. The mixture is shaken round and filtered. In presence of the ink-berry

¹ *Comptes rend.*, 1886, 102, 52.

² *Staz. speriment. agr. Ital.*, 1898, 31, 490.

³ *Atti della R. Stazione Chimico-Agraria Sperimentale de Palermo*, 1881, 1884, 1886, p. 55.

⁴ *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1895, 11, 513.

dye the filtrate is coloured red; only the colouring matter of the red beet behaves similarly towards these reagents.

The following tests are carried out with the red-coloured filtrate to identify the dye:—

1. On addition of alkalis the red liquid becomes pure yellow (the other vegetable colouring matters turn green).

2. On addition of a concentrated solution of sodium bisulphite to the liquid acidulated with acetic acid, the red colour persists (the other dyes are at once discharged).

3. On shaking out with amyl alcohol no trace of the colour goes into the amyl alcohol.

The addition of cherry wine to red wine may sometimes be detected by testing for hydrocyanic acid, as follows:—From 25 c.c. of the wine 2 c.c. are distilled off and tested with tincture of guaiacum and copper sulphate; a blue coloration shows the presence of hydrocyanic acid.¹

14. Estimation of the Total Tartaric Acid, Free Tartaric Acid, Tartar, and Tartaric Acid combined with Alkaline Earth Metals.

(a) *Estimation of the Total Tartaric Acid.*

To 100 c.c. of the wine placed in a beaker are added 2 c.c. of glacial acetic acid, 0.5 c.c. of a 20 per cent. solution of potassium acetate solution, and 15 g. of pure powdered potassium chloride which is dissolved as far as possible by stirring; 15 c.c. of alcohol (95 per cent. by volume) are then added. After the separation of the tartar has been started by rubbing the side of the beaker continuously with a glass rod for a minute, the mixture is allowed to stand at the ordinary temperature for at least fifteen hours, when the crystalline precipitate is removed by filtration. For this purpose either a Gooch platinum or porcelain crucible with a thin layer of asbestos covered with a platinum gauze of at least $\frac{1}{2}$ mm. mesh, or a Witt porcelain filter-plate covered with paper filtering medium, is used; in either case the liquid is sucked through with the filter-pump. The precipitate is washed with a mixture of 15 g. of potassium chloride, 20 c.c. of alcohol (95 per cent. by volume), and 100 c.c. of distilled water, the beaker rinsed about three times with a few cubic centimetres of this solution and drained well after each rinsing, and the filter and precipitate washed about three times by rinsing and pouring on the washing liquid, of which not more than 20 c.c. in all must be used. The precipitate on the filter is then washed back with boiling distilled water, free from alkali, into the beaker and the solution obtained heated to boiling and titrated hot with $N/4$ alkali solution, sensitive blue-violet litmus paper being used as the indicator.

¹ K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 817.

Calculation.—If a cubic centimetres of $N/4$ alkali were used in the titration, then :—

$x = 0.0375 (a + 0.6)$ g. total tartaric acid are contained in 100 c.c. of the wine.

(b) *Estimation of the Free Tartaric Acid.*

50 c.c. of an ordinary, completely fermented wine, or 25 c.c. of a wine containing considerable quantities of sugar, are incinerated in the manner described in No. 4 (p. 764) in a platinum basin. To the ash are carefully added 20 c.c. of $N/4$ hydrochloric acid, and 20 c.c. of distilled water, and the mixture heated over a small flame until boiling begins. The hot liquid is then titrated with $N/4$ alkali, sensitive blue-violet litmus paper being used as indicator.

Calculation.—If a cubic centimetres of the wine were taken, and b c.c. of $N/4$ alkali required for titration, and the wine contains c grams of total tartaric acid per 100 c.c. (determined by No. 14 (a)) then :—

$x = c - \frac{3.75(20 - b)}{a}$ g. of free tartaric acid are contained in 100 c.c. of the wine.

(c) *Estimation of the Tartar.*

50 c.c. of an ordinary, completely fermented wine, or 25 c.c. of a wine containing considerable quantities of sugar, are incinerated in the manner described under No. 4 (p. 764) in a platinum dish. The ash is extracted with hot distilled water, the solution filtered through a small filter, and the dish and filter carefully washed out with hot water. To the aqueous extract of the ash is carefully added 20 c.c. of $N/4$ hydrochloric acid, and the solution heated to incipient boiling over a small flame. The hot solution is then titrated with $N/4$ alkali, sensitive blue-violet litmus paper being used as the indicator.

Calculation.—If d cubic centimetres of wine were taken and e cubic centimetres of $N/4$ alkali used for the titration, and the wine contained c grams of total tartaric acid in 100 c.c. (found by No. 14 (a)), the value of n is first calculated from the equation :—

$$n = 26.67c - \frac{100(20 - e)}{d}.$$

(α) If n is zero or negative, all the tartaric acid is present as tartar in the wine ; then :—

$x = 1.2533 \times c$ grams of tartar are contained in 100 c.c. of the wine.

(β) If n is positive, then :—

$x = \frac{4.7(20 - e)}{d}$ grams of tartar are contained in 100 c.c. of the wine.

(d) *Estimation of the Tartaric Acid in Combination with Alkaline Earth Metals.*

The amount of tartaric acid in combination with alkaline earth metals is calculated from the figures found in the estimation of tartar under No. 14 (c). If c , d , and e have the same significance as they have there, and:—

(α) If n is zero or negative, then the wine contains no tartaric acid in combination with alkaline earth metals.

(β) If n is positive, and free tartaric acid was found, then there are:—

$$x = \frac{3.75(e-b)}{d}$$
 grams of tartaric acid in combination with alkaline earth metals in 100 c.c. of the wine.

(γ) If n has been found to be positive, and free tartaric acid is not present, then:—

$$x = c - \frac{3.75(20-e)}{d}$$
 grams of tartaric acid are in combination with alkaline earth metals in 100 c.c. of the wine.

Note.—The considerations on which the above formulæ are based would require too much space for their elaboration here; they are dealt with in works dealing especially with the analysis of wines.¹

It may, however, be pointed out that:—(α) In the estimation of the total tartaric acid any free tartaric acid is converted into tartar by the addition of potassium acetate, crystallised out, filtered, and titrated; the factor 0.6 in the formula for a is a correction for the solubility of tartar in the washing liquid. (β) The free tartaric acid is that portion of the total tartaric acid not combined as acid salts (bitartrates) by the total alkalinity of the ash. (γ) That quantity of tartaric acid is reckoned as tartar which corresponds to the water-soluble alkalinity, as far as the total tartaric acid present allows. (d) The tartaric acid remaining after deduction of the free tartaric acid and tartar from the total tartaric acid is taken as the tartaric acid combined as alkaline earth salts; it corresponds to the water-insoluble alkalinity of the ash, as far as the total tartaric acid present allows.

With a high content of tartaric acid 0.5 c.c. of a 20 per cent. potassium acetate solution is not sufficient; according to Kulisch, the presence of large quantities of sulphate in the wine hinders the precipitation of tartar. In the treatment of musts 20 c.c. of alcohol instead of 15 c.c. are added; the method is in any case less trustworthy than for wines with normal acid content. The separation of the water-soluble and water-insoluble ash alkalinity is also uncertain, because

¹ Cf. *Die chemische Untersuchung und Beurteilung des Weines*, by K. Windisch, pp. 129-132; Borgmann's *Anleitung zur chemischen Untersuchung des Weines*, by W. Fresenius, pp. 39-45.

of the solubility of certain ash constituents in hot water,¹ as is indeed the whole basis of the method of calculation.

The method is due to A. Halenke, and W. Möslinger,² and has been thoroughly investigated by P. Kulisch;³ numerous other methods which have been proposed for the estimation of free tartaric acid and tartar in wine are inaccurate.

15. Estimation of Sulphuric Acid in White Wines.

The method given under No. 5 (p. 765), for the estimation of sulphuric acid in red wines applies also to white wines.

16. Estimation of Sulphurous Acid.

The estimation of sulphurous acid is carried out in a 400 c.c. distilling flask provided with a doubly-bored stopper carrying two glass tubes, one reaching to the bottom of the flask, the other terminating in the neck and leading to a Liebig condenser; a bulb U-tube (Peligot tube) is attached by means of a perforated stopper to the lower end of the condenser.

Carbon dioxide is led through the tube reaching to the bottom of the flask until the air in the flask is completely displaced; 50 c.c. of iodine solution, prepared by dissolving 5 g. of pure iodine and 7.5 g. of potassium iodide in water, and diluting to 1 litre, are placed in the U-tube, the stopper of the distilling flask is raised, and 100 c.c. of the wine are allowed to flow into the flask from a pipette, without interruption of the current of carbon dioxide. After the addition of 5 g. of syrupy phosphoric acid the wine is carefully distilled, the current of carbon dioxide being maintained until one-half has come over.

The iodine solution, which must have retained its brown colour, is then transferred to a beaker, the U-tube rinsed well with water, hydrochloric acid added, the liquid heated for a short time, and the sulphuric acid produced by the oxidation of the sulphurous acid precipitated with barium chloride. The precipitate of barium sulphate is further treated in the manner described under No. 5.

Calculation.—If a grams of barium sulphate are found on weighing, then there are:—

$$x = 0.2748 \times a \text{ grams of sulphurous acid (SO}_2\text{) in 100 c.c. of the wine.}$$

The total sulphurous acid in the wine can also be determined as follows:—25 c.c. of a solution containing about 56 g. of potassium hydroxide per litre are placed in a flask of about 200 c.c. capacity, and 50 c.c. of the wine added from a pipette, the lower end of which

¹ P. Kulisch, *Z. angew. Chem.*, 1899, 12, 6; W. Fresenius and L. Grünhut, *Z. anal. Chem.*, 1899, 38, 47.

² *Z. anal. Chem.*, 1894, 34, 279.

³ *Z. angew. Chem.*, 1898, 11, 1143.

is immersed in the potassium hydroxide solution while the wine is being run in. After the mixture has been carefully agitated by imparting to it a rotary motion, it is allowed to stand for fifteen minutes; 10 c.c. of dilute sulphuric acid (1 : 3) and a few cubic centimetres of starch solution are added, and the liquid titrated with $N/50$ iodine solution. The iodine solution is added rapidly, but cautiously, until the blue colour persists for a short time after shaking by rotation four or five times.

Calculation of the Total Sulphurous Acid.

If a cubic centimetres of $N/50$ iodine solution are required for 50 c.c. of the wine, then :—

$x = 0.00128 \times a$ grams of total sulphurous acid (SO_2) are contained in 100 c.c. of the wine.

According to recent investigations, a portion of the sulphurous acid in wines is combined with organic constituents, while another portion is present either in the free state or as bisulphite. The estimation of the free sulphurous acid is carried out by the following method :— Carbon dioxide is led through a 100 c.c. flask for ten minutes; 50 c.c. of the wine are then taken from the freshly uncorked bottle by means of a pipette, and allowed to flow into the flask filled with carbon dioxide. After the addition of 5 c.c. of dilute sulphuric acid the liquid is titrated in the manner described above with $N/50$ iodine solution.

The difference between the total sulphurous acid and the free sulphurous acid gives the amount of sulphurous acid in the wine combined with organic constituents.

If the total sulphurous acid was determined by the method described above, this should be mentioned. It is desirable that in any case the free sulphurous acid, or that combined with organic constituents, should be estimated.

Note.—The sulphurous acid finds its way into the wine from the sulphuring of the casks, and of the wine itself. On storage it remains unaltered only to a very small extent; a portion is oxidised to sulphuric acid, but the greater part goes into combination with the aldehydes contained in every wine, and with the sugar in full-bodied wines, in which case it is not directly oxidised by iodine.¹

17. Estimation of Saccharin.

For this estimation 100 c.c. of the wine are evaporated in a porcelain basin on the water-bath, with the addition of coarse, well-washed sand; the residue is extracted, after addition of 1-2 c.c. of 30 per cent. phosphoric acid solution, with a mixture of equal volumes

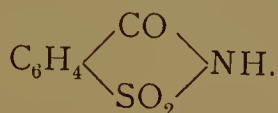
¹ Cf. W. Kerp, *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1904, 21, 141.

of ether and petroleum spirit at a moderate temperature, the mass being continually broken up during this extraction. The extract is filtered through purified asbestos into a flask, and the extraction continued until the filtrate amounts to 200-250 c.c. The greater part of the mixture of ether and petroleum spirit is then distilled off on the water-bath, the residue transferred to a porcelain dish, the flask rinsed out with ether, the ether and petroleum spirit evaporated off completely, and the residue taken up with dilute sodium carbonate solution. The solution is filtered into a platinum dish, evaporated to dryness, the dry residue mixed with four or five times the quantity of solid sodium carbonate, and the mixture gradually added to molten potassium nitrate. The white melt is dissolved in water, carefully acidulated with hydrochloric acid in a beaker covered by a watch-glass, and the sulphuric acid derived from the saccharin precipitated with barium chloride as described in No. 5 (p. 765).

Calculation.—If in the working up of 100 c.c. of the wine a grams of barium sulphate were obtained, then there are:—

$$x = 0.7857 \times a \text{ grams of saccharin in 100 c.c. of the wine.}$$

Note.—The sweet constituent of commercial saccharin is the *o*-sulphimide of benzoic acid, or *o*-sulphobenzimide.



Before proceeding to the estimation of saccharin, its presence in the wine should first be ascertained. For this purpose the residue from the evaporation of the wine obtained as described is extracted with the mixture of ether and petroleum spirit, the extract evaporated and the residue tested for saccharin; several methods may be used for this purpose.

1. *Taste.*—Saccharin may be recognised in very small quantities by its intensely sweet taste. The sweet taste is not, however, a certain indication of the presence of saccharin, as any dulcin present is also extracted from the wine.

2. By conversion of the saccharin into salicylic acid, and detection of the latter by the method of C. Schmidt and Pinette.¹ Sodium hydroxide solution is added to the residue, the mixture dried on the water-bath, and the residue heated for thirty minutes in an oil-bath or air-bath to 250°; the saccharin is thus converted into salicylic acid. The residue is dissolved in water, the solution acidified with sulphuric acid, shaken out with ether, the ether completely removed by evaporation, and the residue tested by means of ferric chloride solution for

¹ *Repert. analyt. Chemie*, 1887, 7, 437.

salicylic acid. If the wine contains salicylic acid, the method is, of course, inapplicable. If potassium hydroxide is used instead of sodium hydroxide, no salicylic acid is obtained from the saccharin.

If only small quantities of sulphuric acid are found by the official method, it must not be concluded that saccharin is present, since other sulphur-containing extractives may occasionally find their way into the ethereal extract; in this case the qualitative detection of saccharin is alone definite. The reagents used should be tested for sulphuric acid.

18. Detection of Salicylic Acid.

To 50 c.c. of the wine are added 50 c.c. of a mixture of equal volumes of ether and petroleum spirit, and the liquid shaken so as to mix the liquids sufficiently, but not enough to cause the formation of an emulsion. The mixture of liquids is then placed in a separating funnel, the layer of ether and petroleum spirit syphoned off, filtered through a dry filter, the ethereal mixture evaporated off on the water-bath, and a few drops of ferric chloride solution added to the residue. A reddish-violet coloration shows the presence of salicylic acid.

If a black or dark brown coloration is obtained, a few drops of hydrochloric acid are added to the mixture, which is then taken up with water, the solution again extracted with a mixture of ether and petroleum spirit and the extract treated as described above.

Note.—For the quantitative estimation of salicylic acid, *cf.* the work of W. Fresenius and L. Grünhut¹ and of J. Messinger.²

19. Detection of Gum Arabic and of Dextrin.

To 4 c.c. of the wine are added 10 c.c. of alcohol of 96 per cent. by volume. If only a slight turbidity is produced, settling as a flocculent precipitate, neither gum nor dextrin is present. But if a clotted, tough precipitate is formed, partly settling on the bottom, and partly adhering to the walls of the vessel, the wine must be tested by the following method:—

100 c.c. of the wine are evaporated to about 5 c.c., and alcohol of 90 per cent. by volume added as long as any precipitate forms. After two hours the precipitate is filtered off, dissolved in 30 c.c. of water, and the solution transferred to a flask of about 100 c.c. capacity. 1 c.c. of hydrochloric acid of sp. gr. 1.12 is added, the flask closed by a stopper carrying a tube 1 m. in length and open at both ends, and the mixture heated for three hours on a boiling water-bath. After cooling, the mixture is rendered alkaline with a solution of sodium carbonate diluted to a definite volume, and the sugar estimated by the method given under No. 10 (p. 767) with Fehling's solution. The sugar is formed

¹ *Z. anal. Chem.*, 1899, 38, 292.

² *J. prakt. Chem.*, 1900 [2], 61, 237.

from any added dextrin or gum arabic; wine without these additions, when treated in the manner described, gives, at most, traces of a sugar reaction.

Note.—Dextrin and gum are differentiated by the fact that gum arabic is lævo-rotatory, while dextrin is strongly dextro-rotatory; gum arabic is precipitated from its solutions by lead acetate, while dextrin is not.

20. Estimation of Tannin.

(a) *Approximate Method of Estimation.*

In 100 c.c. of wine, freed from carbonic acid, the free acids are neutralised down to 0.5 g. in 100 c.c. of the wine by means of a standard alkali solution, if the estimation by No. 6 (p. 765) shows this to be necessary. After the addition of 1 c.c. of 40 per cent. sodium acetate solution, a 10 per cent. ferric chloride solution is added, drop by drop, until no further precipitate is produced. One drop of ferric chloride precipitates 0.05 g. of tannin.

(b) *Estimation of the Content of Tannin.*

The estimation of tannin may be effected by one of the usual methods; the method used should be stated.

Note.—For the determination of the tannin the following are the chief methods used:—

1. Estimation of tannin and colouring matter by the oxidation method of Löwenthal. This is at present the best method, and the one most recommended; it is described in the section on "Vegetable Tanning Materials," this Vol., pp. 453 *et seq.*

(2) Colorimetric estimation of the tannin; M. Barth's method.¹ As a modification of an older method by Nessler and Barth,² a colorimetric method for the estimation of tannin is recommended by Barth. As a standard, a solution containing 0.05 g. of purest tannin, 0.20 g. of acetic acid, and 6 g. of alcohol in 100 c.c. is used. An alcoholic liquid is then prepared from grape-seeds, containing 0.2 g. of acetic acid in 100 c.c., and giving with 10 per cent. ferric chloride solution (5 drops to 10 c.c. of liquid) the same coloration as the previously mentioned tannin solution. This liquid is diluted, maintaining the proportion of 0.2 g. of acetic acid per 100 c.c., to form a series of standards for comparison. The wine under investigation is so far neutralised with sodium hydroxide that its acidity is only 0.2 g. in 100 c.c. If the wine contains more than 0.05 g. of tannin in 100 c.c., it is proportionately diluted; in that case, the acid content must be raised, if necessary, to 0.2 g. in 100 c.c. The colorimetric estimation is carried out in special tubes.

¹ *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 115.

² *Z. anal. Chem.*, 1893, 22, 515.

21. Estimation of Chlorine.¹

50 c.c. of the wine are made alkaline and incinerated; the chlorine is determined gravimetrically in the ash as silver chloride.

22. Estimation of the Phosphoric Acid.

50 c.c. of the wine are evaporated with 0.5 to 1 g. of a mixture of 1 part of potassium nitrate and 3 parts of sodium carbonate in a platinum basin. The residue is carbonised, the carbon extracted with dilute nitric acid, the extract filtered off, the carbon repeatedly washed, and finally incinerated with the filter. The phosphoric acid in the ash is precipitated with molybdate solution and weighed as magnesium pyrophosphate (*cf.* Vol. II., pp. 389 *et seq.*).

Note.—Sweet wines, the direct incineration of which with sodium carbonate and potassium nitrate is inconvenient, may, according to a suggestion of W. Fresenius,² be sown with a trace of pure wine yeast and fermented; the fermented liquid is evaporated with its sediment and then incinerated with sodium carbonate and potassium nitrate. The destruction of the organic constituents of sweet wines by boiling with nitric acid, or nitric acid and sulphuric acid, with subsequent estimation of the phosphoric acid without incineration, has repeatedly been suggested.³ Opinions on this method differ considerably.⁴ The ammonium citrate or citric acid method used for the estimation of phosphoric acid in manures (Vol. II., pp. 393 *et seq.*) has also been suggested, but is not to be recommended.

23. Detection of Nitric Acid.

1. In White Wines.

(a) The alcohol is removed from 10 c.c. of the wine, which is then decolorised with animal charcoal, and filtered. A few drops of the filtrate are allowed to flow into a porcelain dish containing some grains of diphenylamine moistened with 1 c.c. of concentrated sulphuric acid, in such a manner that the two liquids lie side by side. If a blue

¹ For the text of the official instructions, *cf.* *Die Chemische Untersuchung und Beurteilung des Weines*, by K. Windisch, p. 148 (chlorine) and 149 (phosphoric acid). For the mode of carrying out the phosphoric acid estimation, *cf.* also R. Woy, *Chem. Zeit.*, 1897, **21**, 471; 1901, **25**, 292; *Zeitschr. öffentl. Chem.*, 1901, **7**, 415; A. Sartori, *Chem. Zeit.*, 1901, **25**, 263.

² *Z. anal. Chem.*, 1889, **28**, 67.

³ László, *Chem. Zeit.*, 1894, **18**, 1771; *Z. angew. Chem.*, 1897, **10**, 177; R. Wirth, *Chem. Zeit.*, 1895, **19**, 1786; F. Glaser u. K. Mühle, *Chem. Zeit.*, 1896, **20**, 273; W. Thörner and R. Uster, *Forschungsberichte über Lebensmittel*, 1897, **4**, 55; F. Glaser, *Z. Unters. Nahr. u. Genussm.*, 1898, **1**, 553.

⁴ E. von Raumer, *Z. Unters. Nahr. u. Genussm.*, 1898, **1**, 51, 623; W. Fresenius, *Z. anal. Chem.*, 1898, **37**, 223; *Z. Unters. Nahr. u. Genussm.*, 1898, **1**, 766; C. Amthor, *Z. Unters. Nahr. u. Genussm.*, 1898, **1**, 815.

coloration is formed at the surface of contact, the wine contains nitric acid (*cf.* Vol. I., p. 751).

(*b*) For the detection of smaller quantities of nitric acid not recognisable by the above test, 100 c.c. of the wine are concentrated in a porcelain basin on the water-bath to a thin syrup, and absolute alcohol added, after cooling, as long as any precipitate is formed. The precipitate is filtered off, the filtrate concentrated until all the alcohol is driven off, the residue treated with animal charcoal and water, the mixture concentrated to about 10 c.c., filtered, and then tested according to (*a*).

2. *In Red Wines.*

To 100 c.c. of red wine are added 6 c.c. of lead acetate solution, and the mixture filtered; 4 c.c. of a concentrated solution of magnesium sulphate, and a small quantity of animal charcoal are added to the filtrate. After standing and filtering, the filtrate is tested according to 1 (*a*). If no blue coloration results, the filtrate is treated by the method given under 1 (*b*).

All the substances used, including water and animal charcoal, must previously be tested for nitric acid; none containing nitric acid may be used.

This method is not applicable to musts and sugary wines. In the case of such wines, H. Kaserer¹ precipitates the sugar with lime and alcohol (as in estimating glycerol in sweet wines), and tests the filtrate.

24 and 25. Detection of Barium and of Strontium.

100 c.c. of the wine are evaporated down, and incinerated in the manner described in No. 4 (p. 764). The ash is taken up with hydrochloric acid, filtered, and the filtrate evaporated to dryness. The dry salts are tested spectroscopically for barium and strontium. If barium or strontium are present, they should be estimated quantitatively.

26. Estimation of Copper.

The copper is determined electrolytically in $\frac{1}{2}$ to 1 litre of the wine. The metal separating on the platinum electrode is dissolved in nitric acid after weighing, and tested in the usual manner for copper.

A method for the electrolytic estimation of small quantities of copper in wine has been described by T. Frühauf and J. Ursic.² For the estimation of considerable quantities of copper, the wine is incinerated, and the copper determined in the ash.

¹ *Zeitschr. f. landw. Versuchswesen Österreich*, 1903, 6, 197.

² *Cf.* K. Portele, *Bericht des III. österreich. Weinbaukongresses*, 1887, p. 66.

C.—OTHER METHODS OF ANALYSIS.

27. Detection of Foreign Colouring Matter in White Wines.

(a) *Detection of Caramel.*

P. Carles¹ adds albumin solution to the white wine, and filters; if caramel is absent, the filtrate is considerably paler in colour than the original wine, since the natural colouring matter of the wine is precipitated by albumin. Albumin does not precipitate caramel, and thus produces no appreciable loss of tint in the wine. According to the method of C. Amthor,² caramel is precipitated by paraldehyde. The aqueous solution gives a red-brown amorphous precipitate with phenylhydrazine hydrochloride.

(b) *Detection of Coal-Tar Colours.*

The detection of coal-tar colours in white wine is effected by the same method as that used for red wines; attention should be directed chiefly to brown and yellow (including nitro) dyes. A. J. da Cruz Magalhaes³ has pointed out that caramel gives reactions similar to those of coal-tar colours (solubility in amyl alcohol, etc.); according to A. d'Aguiar and W. A. da Silva⁴ they may, however, be readily distinguished.

28. Estimation of Succinic Acid.

None of the older methods for estimating succinic acid in wine are satisfactory;⁵ nor is a more recent method by J. Laborde and L. Moreau⁶ of a nature to arouse confidence. On the other hand, the method of R. Kunz⁷ deserves attention, although it is somewhat tedious. It depends upon the insolubility of barium succinate in strong alcohol, and the difficulty with which succinic acid is oxidised with potassium permanganate. To carry out this method 150 c.c. of the wine are evaporated on the water-bath down to about 100 c.c., and 4 g., or for red wines 5 g., of powdered baryta are added after cooling is complete. After the addition of 3 c.c. of barium chloride solution (1:9) the liquid and precipitate are introduced into a 150 c.c. graduated flask, made up to the mark and filtered; 100 c.c. of the filtrate are then heated in a flask under a reflux condenser for ten minutes, when the liquid foams strongly at first. After cooling, a current of carbon dioxide is led in, the contents of the flask transferred to a porcelain dish and evaporated to a syrup on the water-bath. The residue is taken up with

¹ *J. pharm. Chim.*, 1875 [3], 22, 127.

³ *Comptes rend.*, 1896, 123, 896.

⁵ Cf. *Die chem. Untersuchung und Beurteilung des Weines*, by K. Windisch, p. 191.

⁶ *Annal. Institut. Pasteur*, 1899, 13, 657.

² *Z. anal. Chem.*, 1885, 24, 30.

⁴ *Ibid.*, 1897, 124, 408.

⁷ *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 721.

20 c.c. of water, 80 c.c. of alcohol of 95 per cent. by volume added with stirring, the precipitate filtered off at the pump after standing for two hours, washed well with alcohol, washed back with a small quantity of hot water into the dish, stirred up with about 50 c.c. of water and heated on the water-bath with 15 c.c. of dilute sulphuric acid (1:4). A 5 per cent. solution of potassium permanganate is then run into the hot solution until the liquid is coloured dark red, and the red colour persists during a further warming for three to five minutes on the water-bath with frequent stirring. The excess of potassium permanganate is removed by the addition of ferrous sulphate, the liquid with the resulting manganese oxide evaporated to about 50 c.c., the whole transferred to a Schacherl extraction apparatus (Fig. 78) of about 100 c.c. capacity, and extracted with pure alcohol-free ether. After extraction for about fourteen to sixteen hours the ether is distilled off, the residue dissolved in a small quantity of hot water, and filtered when cool through a small filter into a platinum dish, the filtrate evaporated to dryness on the water-bath, the residue dissolved in hot water and titrated with $N/10$ sodium hydroxide, using phenolphthalein as the indicator. As traces of sulphuric acid go into the extract with the succinic acid, and the residue may also contain acetic acid, the actual estimation of the succinic acid is effected with silver nitrate. For this purpose 20-25 c.c. of $N/10$ silver nitrate solution are added to the accurately titrated solution, the whole made up to the mark in a 100 c.c. flask, shaken, filtered, and the excess of silver nitrate titrated back in nitric acid solution with $N/10$ ammonium thiocyanate and iron alum. 1 c.c. of $N/10$ silver nitrate solution corresponds to 0.0059 g. of succinic acid.

This method has recently been modified by C. von der Heide and H. Steiner.¹

29. Estimation of Lactic Acid.

Since it has been recognised that lactic acid is an important constituent of wines, and that in old wine the greater part of the acid consists of lactic acid, its estimation has assumed a considerable importance.² Simultaneously with this recognition various methods for the estimation

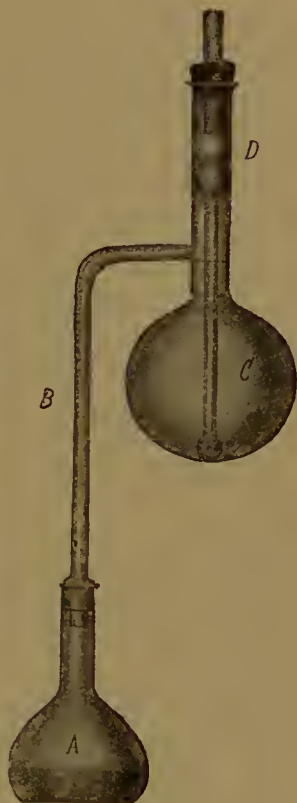


FIG. 78.

¹ *Z. Unters. Nahr. u. Genussm.*, 1909, 17, 291.

² R. Kunz, *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 673; W. Möslinger, *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 1120; *Z. öffentl. Chem.*, 1903, 9, 371; W. Seifert, *Zeitschr. f. landw. Versuchswesen Oesterr.*, 1901, 4, 980, and 1903, 6, 567.

of lactic acid have been worked out. At present no superiority can be assigned to any of the three methods most in use. They all depend upon the solubility of barium lactate in strong alcohol.

(a) *R. Kunz's Method*.¹

In this method 200 c.c. of the wine are evaporated down in a porcelain dish on the water-bath to about two-thirds of the original volume with sufficient powdered barium hydroxide to render the wine alkaline. When cool, the liquid and precipitate are rinsed back into a 200 c.c. flask, filtered, after vigorous shaking, and 160 c.c. of the filtrate evaporated to a thin syrup on the water-bath; during this concentration the barium hydroxide is converted by means of a current of carbon dioxide into barium carbonate. To the residue on evaporation is added an excess of dilute sulphuric acid, the liquid and precipitate rinsed into a Schacherl extraction apparatus (Fig. 78, p. 787), and extracted for thirty-six hours with ether. It is preferable to use an extraction apparatus such as that of Partheil,² in which case eighteen hours are sufficient for the extraction of the lactic acid. About 30 c.c. of water are added to the ethereal extract, and the ether distilled off on the water-bath with repeated shaking. The volatile acids are then driven off from the aqueous solution by means of a current of steam, a distillate of 300-400 c.c. being sufficient in the case of sound wines, while 600-800 c.c. are necessary for acid wines. The residue from the distillation is rinsed into a porcelain dish, a drop of phenolphthalein solution added, and powdered barium hydroxide, until a red coloration is obtained. After fifteen minutes' heating on the water-bath, during which time the alkaline reaction must persist, carbon dioxide is led through the liquid, which is then evaporated down to 10 c.c., washed with 40 c.c. of water into a 150 c.c. flask, and made up to the mark, with vigorous agitation, with alcohol of 95 per cent. by volume. After further vigorous agitation, alcohol is again added up to the mark, and the liquid filtered. The alcohol is evaporated off from 100 c.c. of filtrate, the residue transferred to a beaker, rendered slightly acid with hydrochloric acid, and the barium precipitated hot with sodium sulphate solution. Since the solution contains only barium lactate, the lactic acid can be calculated from the amount of barium obtained as barium sulphate. 1.0 g. of barium sulphate = 0.7714 g. lactic acid.

(b) *W. Möslinger's Barium Chloride Method*.³

The volatile acids are driven off from 80 or 100 c.c. of the wine by means of steam, and barium hydroxide solution added to the

¹ *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 673. ² *Ibid.*, 1901, 4, 1172. ³ *Ibid.*, 1901, 4, 1120.

residue, which is placed in a porcelain dish, until a neutral reaction to litmus paper is obtained. After the addition of 5-10 c.c. of a 10 per cent. barium chloride solution (to convert the organic salts into barium salts) the solution is concentrated to about 25 c.c., neutrality restored by means of barium hydroxide, pure alcohol of 96 per cent. by volume slowly added, with stirring, until the liquid measures 70-80 c.c., the contents of the porcelain basin rinsed with alcohol into a 100 c.c. flask, which is then filled to the mark with alcohol, and the liquid filtered through a pleated filter in a covered funnel. After the addition of a small quantity of water, 80 c.c. of the filtrate are evaporated to dryness in a platinum basin, the residue carefully ignited, and the alkalinity of the ash determined, without heating it until it is white, in the usual manner (*cf.* the estimation of free tartaric acid, p. 777) with $N/4$ hydrochloric acid. The alkalinity of the ash is calculated to cubic centimetres of normal alkali per 100 c.c. of the wine; each cubic centimetre of this ash alkalinity corresponds to 0.09 g. of lactic acid.

(c) *W. Möslinger's Acid Method.*¹

The volatile acids are removed with steam from 50 or 100 c.c. of the wine, 0.2 or 0.4 g. of tartaric acid added to the residue in a porcelain dish, and the whole evaporated down to a few cubic centimetres. To separate the mineral constituents (in the form of tartrates, etc.) the residue is poured into a stoppered 50 c.c. cylinder, rinsing with water until the volume of the aqueous liquid is about 5 c.c., and then with small quantities of alcohol of 95 per cent. by volume, with constant shaking, until the volume of the liquid reaches 30 c.c.; two portions of 10 c.c. each of ether, are then added, with vigorous shaking. The liquid is allowed to settle until it is quite clear, when it is poured off into a porcelain dish, and the insoluble residue rinsed down with ether-alcohol. Water is added, the alcohol and ether evaporated off on the water-bath, the liquid neutralised and further treated as under (*b*), but without the addition of barium chloride.

Möslinger prefers, as a rule, the third method; Windisch has had the most favourable experience with the second.

A. Partheil,² and L. Sostegni, and O. Prandi³ have modified the Kunz method by using a different extraction apparatus. A. Partheil distils the lactic acid in a current of steam, then decomposes it with concentrated sulphuric acid, and measures the evolved carbon monoxide.

¹ *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 1120.

² *Ibid.*, 1901, 4, 1172.

³ *Staz. speriment. agr. Ital.*, 1903, 36, 410.

30. Estimation of Malic Acid.¹(a) *R. Kunz's Method.*²

This method depends upon the quantitative conversion of malic acid into fumaric acid, by means of sodium hydroxide at 120°-130°. The precipitate obtained from 50 or 100 c.c. of the wine, by means of barium hydroxide and alcohol, which contains the organic acids of the wine, is treated in a dish with 10 c.c. of sodium carbonate solution (1:9), and 10 c.c. of sodium hydroxide solution (1:9). After evaporation on the water-bath, the dish with the residue is heated in a drying cupboard for three hours to 120°-130°. The mixture is then dissolved in dilute hydrochloric acid, the liquid rendered alkaline with calcium hydroxide, made up to 150 c.c. in a graduated flask, and filtered; after acidifying with hydrochloric acid, 100 c.c. of the filtrate are extracted with ether in a Schacherl extraction apparatus (see p. 787). In this manner fumaric and succinic acid are obtained, and are estimated together by titration. The fumaric acid is then decomposed by boiling it with potassium permanganate, and the succinic acid estimated as described on p. 786. The difference gives the fumaric acid, from which the malic acid is calculated.

(b) *C. von der Heide and H. Steiner's Method.*³

The tartaric acid is first removed by the official method (p. 776). The filtrate is evaporated to drive off alcohol and acetic acid, and the organic acids converted into barium salts by the addition of barium hydroxide and barium chloride. The malic acid, succinic acid, and barium tannate are precipitated with 80 per cent. alcohol, the precipitated barium salts decomposed with sulphuric acid, and the mixture made into a dry powder with sodium sulphate, and extracted with ether. The ether is evaporated off, the residue dissolved in water, and the tannic acid removed from the solution by means of animal charcoal. After filtration, the succinic acid and malic acid in the filtrate are neutralised, concentrated, incinerated, and the alkalinity of the ash determined. From this the total malic acid and succinic acid are calculated, the succinic acid, determined separately by No. 28 (p. 786), deducted, and the malic acid thus estimated.

¹ *Z. Unters. Nahr. u. Genussm.*, 1902, 5, 1053; *Arch. Pharm.*, 1903, 241, 412.

² For the older methods for the estimation of malic acid (which have not proved satisfactory), cf. *Die chemische Untersuchung und Beurteilung des Weines*, by K. Windisch, p. 182; also, *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 728.

³ *Z. Unters. Nahr. u. Genussm.*, 1909, 17, 307.

31. Detection and Estimation of Citric Acid.

The methods for the estimation of citric acid¹ are still very unsatisfactory, as has been shown by O. von Spindler.² On the other hand, its detection, which is important in wine analysis, has recently been thoroughly and successfully investigated.³ The following methods can be recommended.

(a) *Detection of Citric Acid, by J Schindler's Method.*⁴

To 50 c.c. of the wine ammonia is added until a faint alkaline reaction is obtained, followed by a solution of barium chloride or barium acetate; in the case of wines of low alcohol content, the alcohol is first increased to 12 to 15 per cent. by volume. After standing for four to six hours, or, better, over night, the clear liquid, containing most of the malic acid as the barium salt, is poured off from the precipitate, which is transferred to a filter, and allowed to drain thoroughly without washing. The filter is pierced, and the precipitate, which contains the citric acid as the barium salt, is washed back into the beaker with, at most, 15 c.c. of water. The barium salt is decomposed at the boiling temperature with sulphuric acid (1 : 10), added drop by drop. The liquid is filtered into a test tube, 1-2 c.c. of basic lead acetate solution, and as much saturated lead acetate solution added to the filtrate, which is boiled and filtered whilst hot. If the filtrate on cooling shows a milky turbidity (of lead citrate), citric acid is present. On long standing, lead tartrate may separate in a granular (not milky) form. In this case, the formation of a milky turbidity after boiling up, filtering hot, and cooling, shows the presence of citric acid with certainty. For confirmation the calcium salt of the citric acid is made, and examined microscopically. For this purpose the precipitate of lead citrate is collected on a filter, washed with dilute alcohol, rinsed from the filter with a small quantity of water, the lead precipitated with sulphuretted hydrogen, and the lead sulphide removed by filtration, the filtrate made alkaline with excess of ammonia, concentrated on the water-bath, the residue rinsed into a watch-glass, a small quantity of calcium chloride added, and the mixture allowed to dry completely at a gentle heat. The crystals of ammonium chloride and calcium chloride are dissolved in a few drops of water, and the crystalline residue examined under the microscope.

¹ Cf. *Die chemische Untersuchung und Beurteilung des Weines*, K. Windisch, p. 195.

² *Chem. Zeit.*, 1903, 27, 1263.

³ Cf. W. Möslinger, *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 105; R. Kunz, *ibid.*, 692; G. Paris, *ibid.*, 1901, 4, 160; M. Spica, *Gazz. Chim. Ital.*, 1901, 31, II., 61; W. Seifert, *Bericht der k. k. Versuchsstation, Obst. und Weinbau in Klosterberg*, 1901, p. 3; *Z. Unters. Nahr. u. Genussm.*, 1902, 5, 1180.

⁴ *Zeitschr. f. landw. Versuchswesen, Oesterreich*, 1902, 5, 1053; A. Devarda, *ibid.*, 1904, 7, 6; Bernhard Merk, *Pharm. Zeit.*, 1904, 48, 894.

The calcium citrate formed shows well-defined hone-shaped single crystals, or star-shaped aggregates; calcium tartrate forms prismatic crystals of the rhombic system.

(b) *Detection of Citric Acid by A. Devarda's Method.*¹

To 50 c.c. of the wine from which the alcohol has been removed, and which has been made up again to the original volume, are added 2 c.c., or in the case of blended wines rich in extractives and tannin, 4 c.c. of a 10 per cent. malic acid solution, and the mixture shaken with 1 g., or in the case of blended wines, with $1\frac{1}{2}$ to 2 g. of yellow mercuric oxide for one minute, and at once filtered. 40 c.c. of the filtrate are shaken in a glass cylinder with 6 c.c. of alcohol of 95 per cent. by volume, and 2 c.c. of mercuric nitrate solution, the preparation of which is described below, and placed for a few minutes in water at 10° - 15° . The precipitate is collected on a filter, and, after the liquid has completely drained away, treated on the filter with 15 c.c. of dilute acetic acid (20 c.c. diluted with water to 300 c.c.). Without any stirring of the precipitate the liquid is allowed to drop into a test tube, and is shaken up. 1.5 c.c. of lead acetate solution (7 volumes of cold saturated lead acetate solution with 1 volume of glacial acetic acid) are then added to 10 c.c. of the filtrate in a test tube, the liquid boiled and rapidly filtered. The filtrate is slowly cooled to room temperature, and finally to 10° - 12° . If citric acid is present in the wine a milky turbidity forms which clears with difficulty. In the absence of citric acid the liquid remains clear; at most, a small crystalline precipitate of lead tartrate forms after some time, which is insoluble on warming, and falls at once to the bottom, leaving the liquid clear. The mercuric nitrate solution mentioned above is prepared by adding 2 c.c. of glacial acetic acid to 16 g. of mercuric nitrate in a 100 c.c. flask, dissolving gradually in water, and making up to the mark.

(c) *M. Denigès' Method.*²

10 c.c. of the wine are shaken with 1 g. of lead peroxide and 2 c.c. of mercuric nitrate solution (prepared by dissolving 5 g. of mercuric oxide in 20 c.c. of concentrated nitric acid and 100 c.c. of water), and filtered. A 2 per cent. potassium permanganate solution is then added, drop by drop, until the colour is permanent on heating. Normal wines give only a feeble turbidity. Considerable quantities of citric acid are recognised by the formation of a precipitate.

32. Estimation of the Volatile Esters of Wine.

One quarter of the volume of wine taken for the estimation is distilled off, the distillate exactly neutralised with $N/10$ alkali, alcohol

¹ *Zeitschr. f. landw. Versuchsstation Oesterreich*, 1904, 7, 6.

² *Ann. Chim. anal.*, 1898, 3, 164; *Comptes rend.*, 1900, 130, 32.

and a further measured quantity of $N/10$ alkali added, and the liquid boiled for ten minutes under a reflux condenser; an excess of $N/10$ sulphuric acid is then run in, and the excess titrated back. The volatile esters are calculated as acetic ester.

33. Detection and Estimation of Aldehydes.¹

From 50 c.c. of the wine 20 c.c. are distilled off. The distillate is tested with alkaline potassium mercuric iodide solution, *m*-phenylene diamine hydrochloride, fuchsine and sulphurous acid, and ammoniacal silver solution.

Methods for the estimation of aldehyde have been described by E. Rieter² and by M. Ripper.³

34. Estimation of Dextrose and Lævulose in Musts and in Sweet Wines.

1. *Calculation of the Dextrose and Lævulose from the Polarisation and the Sugar Estimation.*⁴

If the wine contains s grams of reducing sugar per 100 c.c., and its polarisation in a 200 mm. tube at 15° expressed in degrees of angle is d , the wine contains:—

$$L = \frac{0.525s + \alpha}{1.48} \text{ g. lævulose}$$

$$D = s - L \text{ g. dextrose.}$$

The rotation α to be inserted with its proper sign. In the formula, the specific rotation of dextrose is taken as $+52.5$, and that of lævulose as -95.5° at 15° . The process only yields satisfactory results when neither of the sugars is in too great a preponderance; in presence of other optically active substances, such as dextrin, gum, etc., in the wine it is not applicable.

2. *Estimation of Dextrose and of Lævulose by the Volumetric Estimation of the Total Reducing Sugar with Fehling's solution and with Sachsse's solution.*⁵

The sweet wine or must is diluted until the liquid contains about 1 g. of reducing sugar in 100 c.c., the alcohol, and, if necessary, the tannin and colouring matter removed, and the sugar determined

¹ *Die chemische Untersuchung und Beurteilung des Weines*, by K. Windisch, p. 214.

² *Schweiz Wochenschr. Chem. Pharm.*, 1898, 36, 41.

³ *Zeitschr. f. landw. Versuchswesen Oesterreich*, 1903, 6, 26.

⁴ C. Neubauer, *Ber.*, 1877, 10, 827; J. König and M. Karsch, *Z. anal. Chem.*, 1895, 34, 1;

A. Halenke and W. Möslinger, *ibid.*, p. 263.

⁵ F. Soxhlet, *J. prakt. Chem.*, 1880 [2], 21, 227.

volumetrically with both solutions in a definite volume of the diluted liquid, 50 c.c. for example.

If f cubic centimetres of Fehling's solution and s cubic centimetres of Sachsse's solution are used, then there are :—

$D = (0.01257 \times f - 0.00543 \times s)$ g. of dextrose in the quantity used of the diluted wine.

$L = (0.00585 \times s - 0.00845 \times f)$ g. of lævulose in the quantity used of the diluted wine.

From these figures the number of grams of dextrose and of lævulose in 100 c.c. of the wine are then calculated by taking into account the amount of dilution. The presence of cane sugar, glucose, and dextrin is without influence on this method.¹

3. Estimation of Dextrose and Lævulose by Kjeldahl's Method.²

Kjeldahl estimates the reducing power of the total sugar by the use of varying quantities of Fehling's solution (15, 30, 50 c.c.); special Tables calculated by Kjeldahl are employed. The method has been applied, sometimes successfully, sometimes with less success, to the estimation of dextrose and lævulose in sweet wines.³ R. Woy⁴ has combined the new Kjeldahl method with the polarisation, in the same way as Neubauer (*cf.* 1.).

35. Detection and Estimation of Mannitol.

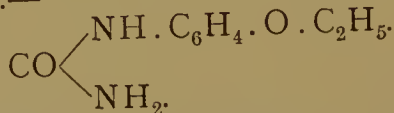
Methods for the detection and estimation of mannitol have been given by U. Gayon and E. Dubourg, Segou, and P. Carles.⁵

36. Detection of Liquorice Juice.

A method proposed by G. Morpurgo⁶ rests upon the detection of the glycyrrhizin contained in liquorice.

37. Detection of Dulcine.

Dulcine, like saccharin, is an artificial sweetening agent; it is *p*-phenetol carbamide :—



¹ *Cf.* J. König and W. Karsch, *Z. anal. Chem.*, 1895, 34, 1; J. König, *Chem. Zeit.*, 1895, 19, 999; M. Barth, *Forschungsberichte über Lebensmittel*, 1896, 3, 20; *Chem. Zeit.*, 1897, 21, 637.

² *Z. anal. Chem.*, 1896, 35, 344, 346.

³ O. Leixl and A. Hilger, *Forschungsberichte über Lebensmittel*, 1897, 4, 135; M. Barth, *Chem. Zeit.*, 1897, 21, 637.

⁴ *Zeitschr. öffentl. Chem.*, 1898, 4, 33.

⁵ *Cf.* *Die chemische Untersuchung und Beurteilung des Weines*, by K. Windisch; also Schidrowitz, *Analyst*, 1902, 27, 42.

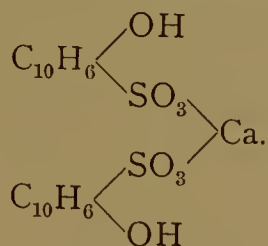
⁶ *Oesterr. Chem. Zeit.* 1899, 2, 361.

For the detection of dulcine in wine, according to G. Morpurgo,¹ 25 g. of lead carbonate are added to 500 c.c. of the wine, and the mixture evaporated on the water-bath to a pasty mass, which is extracted several times with alcohol. The extract is evaporated to complete dryness, the residue extracted with ether, and the ether evaporated off. The residue consists chiefly of dulcine, which is recognised by its sweet taste and by its physical properties. According to the method of J. Berlinerblau,² a portion of the residue is now treated with two or three drops of pure phenol and an equal volume of concentrated sulphuric acid, and the mixture heated to boiling for a short time. When cold, a portion of the thick liquid is poured into a test tube, which is then half filled with water and well shaken; a layer of sodium hydroxide solution or ammonia is then carefully floated upon the liquid, when a blue ring is formed at the surface of contact of the solutions, which gradually becomes more intense, and lasts for several hours. The colour is gradually communicated to the sodium hydroxide solution, which assumes a violet-blue colour, or to the ammonia, which becomes clear blue.

The reaction of A. Jorissen³ for the detection of dulcine is still more characteristic. A portion of the residue is suspended in 5 c.c. of water, 2-4 drops of mercuric nitrate solution added, and the tube placed for five to ten minutes in boiling water; if dulcine is present a faint violet coloration is produced, which is rendered more intense by the addition of a small quantity of lead peroxide. For the preparation of the mercuric nitrate solution 1-2 g. of freshly precipitated mercuric oxide are dissolved in nitric acid, water added, and sodium hydroxide solution in nearly sufficient quantity to redissolve the precipitate formed; the liquid is then diluted to 15 c.c., allowed to settle, and decanted.

38. Detection of Abrastol (Asaprol).

Abrastol, the calcium salt of β -naphthol sulphonic acid:—



has been recommended in France, under the name of abrastol or asaprol, as a preservative for wine. For the detection of this substance,

¹ *Selmi*, 1893, 3, 87.

² *J. prakt. Chem.*, 1884 [2], 30, 103.

³ *Revue Chim. Ind.*, 1896, 7, 134; *J. Soc. Chem. Ind.*, 1896, 15, 620.

according to the method proposed by Sanglé-Ferrière,¹ 200 c.c. of the wine are boiled with 8 c.c. of hydrochloric acid for an hour under a reflux condenser, or, after removal of the alcohol, for thirty minutes over a free flame or for three hours on a water-bath; the abrastol is decomposed with separation of β -naphthol. When cold, the liquid is extracted with 50 c.c. of petroleum spirit, the extract filtered into a dish, and the petroleum spirit evaporated off at the lowest possible temperature. The residue is dissolved in 10 c.c. of chloroform, the solution transferred to a test tube, a fragment of potassium hydroxide and a few drops of alcohol added, and the contents of the tube heated to boiling for two minutes. If abrastol was present in the wine, and consequently β -naphthol in the chloroform solution, a dark blue colour, rapidly turning to green and then yellow, is produced. If the wine contained very small quantities of abrastol, the chloroform has a greenish tint, and only the fragment of potassium hydroxide is coloured blue.

39. Estimation of Nitrogen.²

The estimation of nitrogen is carried out by means of Kjeldahl's method. For ordinary wines, 50 c.c. are evaporated down in the decomposition flask, and the residue treated in the usual manner. Sweet wines and musts are previously fermented, the sweet wines by the addition of a trace of yeast; they are then evaporated down and treated as above.

40. Detection and Estimation of Boric Acid.

(a) *Detection of Boric Acid.*³

50 c.c. of the wine are evaporated down in a platinum dish and the residue ignited. The ash is taken up with 10 c.c. of water, 2 c.c. of hydrochloric acid of sp. gr. 1.124 added, a strip of yellow turmeric paper dipped in the solution and dried on a watch-glass at 100°. If the moistened part of the paper shows, after four to five minutes, a red coloration which is transformed into blue on being moistened with a drop of dilute sodium carbonate solution, boric acid is present in the wine.

(b) *Estimation of Boric Acid.*⁴

The following method depends upon the fact that boric acid, in itself a very weak acid, in the presence of polyvalent alcohols (glycerol,

¹ *Comptes rend.*, 1893, 117, 796; *Rev. intern. falsific.*, 1894, 7, 15.

² Cf. P. Kulisch, *Z. anal. Chem.*, 1886, 25, 149.

³ M. Ripper, *Weinbau und Weinhandel*, 1888, 6, 331.

⁴ K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1905, 9, 641.

mannitol) assumes the character of a strong acid, giving a sharp end-point when titrated with phenolphthalein.¹

After being rendered alkaline, 50 c.c. of wine are evaporated on the water-bath and incinerated (*cf.* p. 764). The ash is completely exhausted with hot water, and the extract filtered, rendered faintly acid with hydrochloric acid, boiled under a reflux condenser for ten minutes to remove the carbon dioxide, and a few drops of phenolphthalein solution added to the cooled liquid, which is then titrated to a distinct pink with *N*/10 barium hydroxide solution; 1-2 g. of pure powdered mannitol are then added, when the pink colour disappears, and *N*/10 barium hydroxide solution added until it is again permanent. A further portion of 0.5 g. of mannitol is then added, and the titration repeated, if the pink colour disappears, until a permanent pale pink colour is obtained. Each cubic centimetre of *N*/10 barium hydroxide solution used after the addition of mannitol corresponds to 0.0062 g. of crystallised, orthoboric acid (H_3BO_3).

41. Detection and Estimation of Fluorine Compounds.

(a) *Detection of Fluorine Compounds by P. Kulisch's Method.*²

Kulisch avoids the use of calcium chloride and such substances which often contain fluorine, by evaporating down 500 c.c. of the wine without any addition, and incinerating. To avoid the vigorous evolution of carbon dioxide on the subsequent treatment with sulphuric acid, the ash is exactly neutralised with dilute sulphuric acid and the solution again evaporated. The ash is then transferred with a platinum spatula to a platinum crucible, the last residues being wiped out with damp, fluorine-free filter paper. After incineration of the paper, the ignited residue in the crucible is covered with the purest concentrated sulphuric acid, and the crucible at once covered with a small flask, the bottom of which is coated with wax in which letters have been scratched. A slow current of water is passed through the flask, which is closed by a double-bored stopper during the whole treatment, to keep it cool. The crucible is heated on an asbestos plate, at first gently and then strongly, for about one hour, until sulphuric acid vapours begin to appear. The etching of the letters proves the presence of fluorine compounds only if they appear of themselves on the cleaned surface of the glass. If they appear only if the glass is breathed upon, the presence of fluorine is uncertain.

¹ L. Barthe, *J. Pharm. Chim.* 1894 [5], 29, 163; Hönig und Spitz, *Z. angew. Chem.*, 1896, 9, 549; G. Jørgensen, *ibid.*, 1897, 10, 5.

² *Cf.* Post's *Chem.-techn. Analyse*, 1907, vol. 2, p. 538; also C. Amthor, *Pharm. Zentrallh.*, 1896, 37, 111; K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 961; P. Kulisch, *Landw. Zeitschr. f. Els.-Lothr.*, 1904, p. 177.

(b) *Estimation of Fluorine by F. P. Treadwell and A. A. Koch's Method.*¹

100 c.c. of the wine are placed in a 250 c.c. flask, and pure 2*N* sodium hydroxide solution added until a faint alkaline reaction is obtained, and then silver nitrate solution until no further precipitate is formed; the solution is well shaken, made up to the mark with distilled water, mixed, and at once filtered through a pleated filter. The first 5-10 c.c. of the filtrate are neglected; 200 c.c. of the subsequent filtrate are collected in a 250 c.c. flask, and sodium chloride solution added in sufficient quantity to precipitate the excess of silver as silver chloride. The solution is then vigorously shaken, made up to the mark with water, allowed to stand for twelve to twenty-four hours, the supernatant, usually clear, liquid withdrawn with a pipette, and 175 c.c. of it taken for the fluorine estimation. If the liquid is not quite clear, it is filtered. The first 5-10 c.c. of the filtrate are neglected, and of the succeeding portion 175 c.c. (=56 c.c. wine) are transferred to a 250 c.c. porcelain dish, 3-4 c.c. of 2*N* sodium carbonate solution added, the liquid heated to boiling, precipitated with a large excess of calcium chloride and boiled, after the precipitation, for five minutes. The precipitate is collected on a filter, washed with hot water until the washings show no reaction for chlorine, and dried. As much as possible of the dry precipitate is brought into a platinum crucible, the filter burnt in a platinum spiral, the ash added to the main precipitate in the crucible, and the whole ignited at a dull red heat for ten to twenty minutes. The crucible is covered with a watch-glass, after the addition of 2-4 c.c. of $\frac{3}{2}$ *N* acetic acid, and allowed to stand in the cold until the evolution of carbon dioxide ceases. It is then heated, covered with the watch-glass, for about forty minutes on the water-bath, the precipitate being broken up from time to time with a platinum spatula or glass rod. The watch-glass is now removed, and the precipitate heated to dryness, moistened with two drops of acetic acid, then with water, and the liquid decanted through a small filter in such a manner that most of the precipitate remains in the crucible and only a small quantity of it reaches the filter. The washing by decantation is continued until the filtrate yields merely a slight turbidity with ammonium oxalate. The filter is then dried, and as much as possible of the precipitate adhering to it added to the main portion in the crucible, which has been dried meanwhile. The filter is burnt in the platinum spiral, and the ash placed in the crucible, which is ignited for a few minutes at a dull red heat, allowed to cool in the desiccator, and weighed. After weighing, the treatment with acetic acid, extraction with water, filtration, drying, and weighing are

¹ *Z. anal. Chem.*, 1904, 43: 491.

repeated, until the loss of weight does not exceed 0.0005 g., the last weighing being used for the calculation of the fluorine in the calcium fluoride. One part $\text{CaF}_2 = 0.4870$ parts fluorine.

A. Kickton and W. Behncke¹ state that the results obtained by this method are considerably too low.

42. Detection of Hydrogen Sulphide.

50 c.c. of the wine are first distilled to half the original volume.

(a) To one portion of the distillate two drops of an alkaline lead solution are added ; in presence of hydrogen sulphide a brown coloration or a dark brown precipitate of lead sulphide is formed.

(b) *The Nitroprusside test for Hydrogen Sulphide.*—The distillate from the wine is made alkaline, and a drop of sodium nitroprusside solution added. The appearance of an unstable violet coloration which soon loses its tint, shows the presence of hydrogen sulphide.

The simplest method is to place 25-50 c.c. of the wine in a conical flask, in the neck of which a strip of lead paper is hung, and to warm the wine. If the wine contains hydrogen sulphide the paper is coloured brown.

43. Estimation of Lime, Magnesia, Alkali Metals, Silicic Acid, Iron, Alumina, Manganese, Heavy Metals, and Arsenic.

The estimation of these inorganic constituents is effected by the ordinary methods of quantitative analysis. An exact description of the methods suitable for the examination of wines will be found in *Die chemische Untersuchung und Beurteilung des Weines*, by K. Windisch, pp. 241-251.

44. Detection of Oxalic Acid.

According to H. Fonzes-Diacon² the practice has arisen of treating certain white wines with 18 to 20 g. of oxalic acid per hectolitre, to prevent turbidity (*casse blanche*). The presence of oxalic acid may be detected by treating 100 c.c. of the wine with 5 c.c. of glacial acetic acid and 5 g. of sodium acetate, allowing to stand for twenty-four hours, collecting the precipitate and examining it in the usual way for oxalic acid. A wine free from oxalic acid when treated similarly is stated to remain clear for three days.

¹ *Z. Unters. Nahr. u. Genussm.*, 1910, 20, 193.

² *Ann. Falsific.*, 1914, 7, 22 ; *J. Soc. Chem. Ind.*, 1914, 33, 213.

II. THE JUDGING OF WINES FROM THE RESULTS OF THE CHEMICAL EXAMINATION.

In forming an opinion on a wine a distinction must be made between the two following cases:—

1. Substances have been added to the wine which are completely foreign to a normal wine, such as coal-tar colouring matters, certain preservatives, saccharin, dulcine, etc. These substances are almost without exception easily and certainly detected, and an opinion upon wines containing them is generally easily given.

2. Substances or mixtures of substances which are normally present in wine have been added, such are glycerine, tartar, alcohol, etc. The qualitative detection of such substances is obviously insufficient; it is necessary to know the quantity present in order to form an opinion as to whether or not they have been added to the wine, and for this purpose the quantities present in an unadulterated wine must be known. A very large amount of information on the chemical composition of pure wine from German wine-growing districts has been collected by the "Commission for the preparation of the wine statistics of Germany" (Kommission zur Bearbeitung einer Weinstatistik für Deutschland) which have considerably facilitated the valuation of German wines.¹

The Recognition of Sugared Wines.

If water containing much nitric acid was used for dissolving the sugar, the nitric acid content of the wine serves as an indication of the addition of sugar. Small quantities of nitric acid may be introduced into the wine by the washing of the casks with water containing nitrates;² moreover, many musts and wines naturally contain traces of nitrates.³ The nitric acid in wines gradually decreases and finally disappears,⁴ so that even if water containing much nitrate has been added, the method becomes valueless after the lapse of time.

If the district, the position of the vineyard, and the vintage, or alleged vintage of a wine, are known, it is often possible by a comparison of the composition of the wine under consideration with that of the pure wine from the same district, position of vineyard, and vintage, to determine whether sugar has been added, and approximately how much. The wine statistics of Germany afford a valuable standard of comparison for this purpose.

¹ These wine statistics were formerly published annually in the *Z. anal. Chem.* Since 1901 they have been published in the *Arbeiten a. d. Kaiserlichen Gesundheitsamte.*

² Cf. E. Egger, *Arch. Hyg.*, 1884, 2, 373; E. Pollak, *Chem. Zeit.*, 1887, 11, 1465, 1623.

³ Cf. W. Seifert u. H. Kaserer, *Zeitschr. f. landw. Versuchswesen Oesterr.*, 1903, 6, 555.

⁴ Cf. J. Herz, *Rep. anal. Chem.*, 1886, 6, 360; E. Borgmann, *Z. anal. Chem.*, 1888, 27, 184; W. Seifert, *Oesterr. Chem. Zeit.*, 1898, 1, 285.

Earlier data on the recognition of over-sugared wines—as, for example, the acid residue of W. Möslinger,¹ and the tests of L. Grünhut²—are no longer applicable, in view of the much smaller extent to which the addition of sugar is now carried on.

“Marc” Wines.

In consequence of their mode of preparation (fermentation of a sugar solution over the grape skins, or marc) these wines are generally poor in extractives, free acids, and nitrogen, but rich in tannin, and frequently also in mineral matter, particularly potash and lime, but are lacking in phosphoric acid.

For their recognition, the most important feature is the high content of tannin. It is, however, to be borne in mind, that fining with gelatin or albuminous substances can be pushed until a large part of the tannin has been removed. The tannin in genuine white wines is often not inconsiderable in amount, especially when the wine has remained for long in contact with the marc, and has been partly or wholly fermented on it; in this case, however, the extract is correspondingly high, since the fermenting must is able to remove more extractives from the marc on long contact. An adulteration with wine made from marc is therefore not proved by a high content of tannin alone; the other factors mentioned must also be taken into consideration.³

M. Barth⁴ found that the portion of the extract originating in the skins in the case of wines fermented on the marc is at least five times the amount of the tannin; wines which show less than 1.5 g. of extract per 100 c.c. after deduction of five times the tannin from the total extract are, according to Barth, either wines made from marc wines adulterated with these, or wines which have been fermented in contact with the skins for an undue length of time. W. Fresenius and L. Grünhut⁵ regard the factor 5 as too high. They observed that marc wines seldom contain tartaric acid combined with the alkaline earth metals, but mostly only tartar. This characteristic is eliminated by the addition of tartaric acid and strong sulphuring.

Yeast Wines.

Yeast wines usually contain little extract and acid, but often much inorganic matter and nitrogen.

Raisin Wines (Basis Wines).

Properly made raisin wine can hardly, in the present state of knowledge, be distinguished by chemical means from wine prepared

¹ *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 93.

² *Ibid.*, 1901, 4, 1161.

³ Cf. J. Stern, *Zeitschr. f. Nahrungsm. Unters. u. Hygiene*, 1893, 7, 409; E. Späth, *Z. angew. Chem.*, 1896, 9, 721.

⁴ *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 103.

⁵ *Z. anal. Chem.*, 1899, 38, 472.

from fresh grapes. It is recognised by its peculiar taste, among other characteristics; it is often rich in volatile acids. Analyses of raisin wine have been made by A. Schneegans.¹

The Addition of Fruit Must and Fruit-Wine to Grape-Wine.²

Cider and perry differ considerably in the pure state from wine from grapes in their chemical composition; the most important difference is that they contain no tartaric acid or tartrates. All other differences are differences of degree; thus cider has usually less alcohol, less acid, more acid-free extract (so-called extract residue), and more mineral constituents, than wine from grapes. In grape-wines adulterated with cider these differences may so far disappear that the various constituents fall within the limits which have been observed for pure natural wines. Even the content of tartar is not conclusive. Sometimes the addition of cider or perry can be detected by the taste.

According to F. F. Mayer,³ grape-wines separate ammonium magnesium phosphate, and cider or perry, calcium phosphate, on the addition of ammonia, and these may be distinguished by their crystal form; the method proposed by J. Formánek and O. Laxa⁴ for examination of mixtures of cider or perry and grape-wines is uncertain. K. Portele⁵ recommends an examination of the sediment of the wine, if possible of the lees; this contains the characteristic starch grain of the apple, etc. Gooseberry, currant, and whortleberry wine are recognised by their containing citric acid. Cherry wine may often be detected by testing the red wine for hydrocyanic acid.⁶

Boric Acid in Wine.

Numerous investigations have shown that nearly all wines contain small quantities of boric acid; F. Schaffer⁷ found in twenty-eight samples of wine from 0.008 to 0.050 g., on the average, 0.029 g. of orthoboric acid (H_3BO_3) per litre. To detect the addition of boric acid a quantitative estimation is therefore necessary.

Soluble Fluorine Compounds in Wine.

It is not yet certain whether natural wines contain traces of fluorine compounds or not. F. Schaffer⁸ found fluorine in natural wines;

¹ *Arch. Pharm.*, 1901, 239, 91, 589.

² Cf. P. Kulisch, *Landwirtschaftl. Jahrb.*, 1890, 19, 83; and W. Seifert *Zeitschr. f. Nahrungsm.-Unters. u. Hygiene*, 1892, 6, 120.

³ *Z. anal. Chem.*, 1872, 11, 337.

⁴ *Z. Unters. Nahr. u. Genussm.*, 1899, 2, 401; cf. also W. Seifert, *Oesterr. Chem. Zeit.*, 1898,

1, 265.

⁵ *Zeitschr. f. landw. Versuchswesen Oesterreich*, 1898, 1, 241.

⁶ K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 817.

⁷ *Schweiz. Wochenschr. Chem. Pharm.*, 1902, 40, 478.

⁸ *Bericht des Kantonchemikers des Kantons Bern*, 1902, p. 2.

F. P. Treadwell and A. A. Koch¹ did not. P. Kulisch² disputes the occurrence of fluorine compounds in natural wines; A. Kickton and W. Behncke,³ on the other hand, found small quantities of fluorine in numerous wines. In any case, the quantities concerned are less than 1 mg. of fluorine in 100 c.c. of wine.

Salicylic Acid in Wine.

Salicylic acid occurs in many wines,⁴ and in many kinds of fruit, especially in raspberries and strawberries,⁵ but always in small quantities, at most 1-2 mg. in 1 kg. of fruit or 1 litre of fruit juice. It often appears to be present as the methyl ester.

Glycerol in Wine.

The amount of glycerol resulting on fermentation varies considerably according to the conditions. It bears a certain ratio to the amount of alcohol. Usually 5-14 parts of glycerol are formed to 100 parts of alcohol. A wine may contain apparently more glycerol than this, when a portion of the alcohol produced by the fermentation disappears. This takes place chiefly:—(1) By long storage in casks; consequently old wines are found to contain relatively more glycerol. (2) By the action of moulds a portion of the alcohol may be oxidised to carbon dioxide. In general a higher alcohol-glycerol ratio (10-14 parts by weight of glycerol, and more, to 100 parts by weight of alcohol) is found only in fine wines which have a higher content of other extractives. Wines subjected to a secondary fermentation and much sweetened often have a lower alcohol-glycerol ratio.

Sodium Salts in Wine.

According to O. Krug,⁶ German wines contain not more than 10 mg. of sodium salts, calculated as Na_2O , in 100 c.c. If more is found, sodium salts have been added to increase the total inorganic constituents.

¹ *Z. anal. Chem.*, 1904, 43, 491.

² Post's *Chem. Tech. Analyse*, 1907, vol. 2, p. 558.

³ *Z. Unters. Nahr. u. Genussm.*, 1910, 20, 193.

⁴ L. Medicus, *Bericht*, 9, *Versamml. d. fr. Verein. bayer. Vertreter d. angew. Chem. in Erlangen*, 1890, p. 42; A. J. Ferreira da Silva, *Ann. Chim. anal.*, 1900, 5, 381; 1901, 6, 11; H. Mastbaum, *Chem. Zeit.*, 1901, 25, 465; 1903, 27, 829; A. Cordoso Pereira, *Bull. Soc. Chim.*, 1901 [3], 25, 475; H. Pellet, *Ann. Chim. anal.*, 1900, 5, 418; 1901, 6, 327, 328; *Bull. Assoc. Chim. Sucr.*, 1902-3, 20, 286; K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1902, 5, 653; M. Spica, *Gazz. Chim. Ital.*, 1903, 33, 482.

⁵ R. Hefelmann, *Zeitschr. öffentl. Chem.*, 1897, 3, 171; Truchon and M. Claude, *Ann. Chim. anal.*, 1901, 6, 85; L. Portes and Desmoulière, *ibid.*, 1901, 6, 401; P. Süß, *Z. angew. Chem.*, 1902, 15, 1041; *Z. Unters. Nahr. u. Genussm.*, 1902, 5, 1201; K. Windisch, *Z. Unters. Nahr. u. Genussm.*, 1903, 6, 447; A. Desmoulière, *Bull. Sciences Pharmacol.*, 1902, 4, 204; F. W. Traphage and E. Burke, *J. Amer. Chem. Soc.*, 1903, 25, 242.

⁶ Cf. *Z. Unters. Nahr. u. Genussm.*, 1905, 10, 417; 1907, 13, 544.

Volatile Acids in Wine.

Normal German white wines contain only small quantities of volatile acids; red wines, in consequence of their mode of preparation, usually contain more. Southern wines and sweet wines are usually rich in volatile acids.¹ Large quantities of volatile acids arise in wines by the action of vinegar bacteria (*Bacterium aceti*) and from other morbid conditions of the wine. In wines with an equal content of volatile acids, acetous fermentation is less noticeable, the more extract and ash they contain, the higher the alkalinity of the ash, and the more the alkalinity exceeds the acidity of the tartaric acid in the wine.²

THE JUDGING OF SWEET WINES.

A distinction must be made between unconcentrated and concentrated wines. Unconcentrated wines are prepared by the addition of alcohol to unfermented or slightly fermented musts, with consequent inhibition of the fermentation ("killing" the yeast), or by the addition of sugar to fermented wines. The concentrated sweet wines are made from dried berries (raisins), or from must concentrated by boiling down, or by evaporation in a vacuum; the dried berries are either pressed separately, or the juice is allowed to run out spontaneously, and fermented, or extracted with ordinary wine or must.

The composition of sweet wines varies considerably with the mode of preparation. The concentrated sweet wines contain sugar, non-fermentable extractives, and mineral constituents in much larger quantities than are found in ordinary wine; they are especially characterised by a high content of phosphoric acid. The unconcentrated sweet wines do not possess this characteristic; they are much nearer in composition, apart from their content of sugar and alcohol, to ordinary wines. The sweet wines obtained by brandying musts contain but little glycerol, since they are hardly fermented at all; the sweet wines made by adding sugar to fermented wine contain an amount of glycerol corresponding to the alcohol produced by the fermentation. Both sugar and alcohol are often added in the preparation of such wines.

In the examination of sweet wines the object is to distinguish the real concentrated sweet wines from the inferior unconcentrated wines, and sometimes to determine the degree of concentration. The characteristics of a concentrated sweet wine are, as mentioned above, a high content of sugar-free extract and of ash, and particularly of phosphoric acid.

¹ Cf. W. Fresenius, *Z. anal. Chem.*, 1897, 36, 118; *Forschungsberichte über Lebensmittel*, 1894, I, 453; A. Borntraeger and G. Paris, *Chem. Zeit.*, 1898, 22, 172.

² W. Müslinger, *Forschungsberichte über Lebensmittel*, 1897, 4, 339.

The Tokay wines and the other Austro-Hungarian concentrated sweet wines have a special position among the concentrated sweet wines. They are concentrated to a greater extent, and are therefore usually richer in sugar-free extract and phosphoric acid than other sweet wines; L. Röseler¹ found for a large number of samples that their content of phosphoric acid is usually at least 0.055 g. per 100 c.c.

Apart from the estimation of the glycerol, the separate estimation of the dextrose and lævulose in sweet wines gives information on the mode of preparation. During fermentation it is the dextrose which is first and chiefly attacked, so that a partially fermented wine contains more lævulose than dextrose. If, therefore, in a sweet wine the lævulose preponderates, it may be assumed that a fermentation, either of concentrated grape-juice, or of the artificially added sugar, has taken place. Sweet wines prepared either by brandying the must, or by adding sugar to a completely fermented wine, or by extracting dried berries with a finished wine, often contain approximately equal quantities of dextrose and lævulose.

The addition of alcohol to many sweet wines is usual, and not to be objected to. Tokay wines are usually not fortified. In consequence of their having been plastered, the sweet and Southern wines often contain much sulphuric acid; they often contain also much volatile acid.² The amount of non-volatile acid is usually not high.

¹ *Z. anal. Chem.*, 1895, 34, 354.

² *Forschungsberichte über Lebensmittel*, 1894, I, 449.

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BREWING MATERIALS AND BEER¹

By ARTHUR R. LING, Lecturer on Brewing and Malting, The Sir John Cass Technical Institute, Aldgate, London, and G. CECIL JONES, A.C.G.I.

THE BREWING PROCESS.

THE essential, and in some countries the only permissible, raw materials of beer are malt, hops, and water; and the brewing process, reduced to its simplest terms, consists in making an aqueous infusion of malt, boiling this with hops, cooling, and fermenting the hopped wort with yeast.

Malt without qualification has come to mean barley malt, which is everywhere the most important raw material of the brewing industry. Oats and wheat are malted to a small extent for use by brewers of special ales and stouts, but the amount of these cereals used is insignificant.

Not all barleys are suitable for malting purposes, and since most brewers make at least a portion of the malt they use, barley must be regarded as one of the raw materials of the industry, and some notes on its examination are included in this section.

Malt is made by steeping barley in water for about three days, spreading it to a depth of a few inches on a floor and allowing it to germinate there for ten or twelve days, moving it from time to time on to a fresh section of the floor, in such a way that it gets uniformly aerated.

The object of malting is as follows. The principal material of barley is starch, which is insoluble and useless as such either to the brewer or the embryo plant. But when the corn is supplied with moisture at not too low a temperature, enzymes are secreted which enable the embryo to draw on the reserve material stored up in the endosperm. On the amylolytic enzyme, diastase, depend the transformations effected in the brewer's mash tun, but other enzymes are developed simultaneously, some of them acting on the nitrogenous constituents of the grain, and one or more of them, whose rôle is of the

¹ This section, as stated in the Preface, has been completely rewritten for the English edition. The corresponding section in the German edition is contributed by Professor C. J. Lintner.

first importance, bringing about a partial dissolution of the cell walls of the endosperm. When this latter process, spoken of as "modification," has been carried far enough, the process of germination is arrested by drying the malt on a kiln over a fire of anthracite or coke and finally "curing" it at a temperature which may finally reach 200°-230° F. When loaded to the kiln, the so-called "green" malt has a number of well-developed rootlets, but the incipient aerial stem or acrospire, though visible through the husk, is never allowed to grow out and produce green leaves. The drying process serves not only to arrest the growth of the malt, but induces partial caramelisation of the cell contents with development of the characteristic malt flavour, considerably restricts the diastatic power, and yields a product which, in order to keep its content of moisture below 3 per cent., must be stored in good bins.

In the brewery, malt is crushed between rolls and mashed with water at a temperature in the neighbourhood of 160° F. The diastase now converts nearly the whole of the starch into soluble substances, among which the sugar, maltose, always predominates. The exact character of the wort depends on a number of factors, among which the character of the malt and the exact mashing temperature are perhaps most important. Generally speaking, higher mashing temperatures will determine the formation of relatively larger proportions of unfermentable or difficultly fermentable substances—dextrins and malto-dextrins.

The sweet wort is run off from the grains, which are exhausted by sparging with hot water, and is then boiled with hops, which confer on it a bitter flavour and keeping properties. It is then cooled and run to the fermenting vessels, where it is gauged and its specific gravity taken for purposes of excise. The specific gravity at this stage, referred to water as 1000, is the true "original gravity" of the resulting beer. The estimation of original gravity from the analysis of finished beer is one of the most frequent operations of the brewing laboratory.

Fermentation with yeast follows, the maltose in the wort being converted into alcohol and carbonic anhydride, together with other changes which may have a profound effect on the finished beer, but the study of which forms no part of the routine of a brewery laboratory.

With the racking of the beer at the close of the primary fermentation, the brewing process may be said to end, but the product is not yet fit for consumption. If stored sufficiently long, a slow secondary fermentation gradually brings it into condition. This secondary fermentation is brought about by the few yeast cells remaining in the beer, probably aided by certain other organisms, and the process is in the case of some beers assisted by the addition of fresh hops, the enzymes of which degrade a portion of the otherwise unfermentable substances in the beer. Strong ales and the finest pale ales are so produced, but

mild ales, porter, and the lighter pale ales are all "running beers." This is the name given by the trade to beers which are artificially brought into condition with a minimum of delay. To effect this, "priming" is resorted to. This may consist of an addition to each barrel of beer of one or two quarts of strong sugar solution, which is readily fermented by the yeast cells remaining in the beer, the latter rapidly acquiring condition.

Since 1880, when the malt tax was repealed and a tax on beer (more exactly on beer wort immediately before fermentation) substituted for it, brewers in the United Kingdom have been allowed to use any saccharine or starchy materials, and this latitude has had much to do with the development of the brilliant light ales of the present day. According to the latest official return, there were used in the United Kingdom in 1912, 966,000 tons of malt, 73,000 tons of unmalted cereals, and 153,000 tons of sugar. Sugar, other than that used for priming, is usually added to the wort in the copper, the sugar in use being raw cane sugar, invert sugar, commercial glucose and other products of the hydrolysis of starch by acids. The caramel used for bringing beers up to some standard tint is also made from glucose and counted as sugar by the Excise. The most popular forms of unmalted cereals are the so-called "flakes." The material of this kind most commonly used is flaked maize, but flaked rice is also employed. The corn after being degermed is submitted to a process of torrification, whereby its starch is rendered amenable to the action of diastase. Such material is mashed with malt in the mash tun, whereas simple degermed maize, known as "grits," has first to be gelatinised in a converter.

I. BREWING MATERIALS.

A.—WATER.

So far as regards its general purity and freedom from organic matters, the same remarks apply to brewing-water as to drinking-water, and the analytical methods described for the latter in the section on "Drinking Water and Water Supplies," Vol. I., pp. 732 *et seq.*, may be adopted for the former.

It should be pointed out that the character of the saline matters present in a water is of much importance in determining its fitness for brewing different kinds of beer. Thus it is held that waters intended for pale ales should contain 60 or more grains per gallon of calcium sulphate and should be free from carbonates; those intended for mild ales should contain 25 or more grains of chlorides; whilst those intended for stouts should contain alkali earth carbonates to the extent of about 12 grs. per gallon and chlorides to the extent of 10-25 grs. per gallon.

Some of the deep-well waters employed for the production of stout in London contain about 10 grs. per gallon of sodium carbonate, a little less of calcium and magnesium carbonates, and about 10 grs. per gallon of sodium chloride.

The presence of more than a minute trace of iron is generally held to be objectionable, and nitrates are said to give rise to yeast weakness. Instances are, however, known to the authors in which waters containing 5 grs. of nitrate (calculated as sodium nitrate) per gallon are used for the production of high-class pale ales.

Saline mixtures are sold for the treatment of waters to render them fit for the production of different beers. These are to be analysed by the ordinary methods of mineral analysis.

B.—MALT.

Methods of malt analysis are necessarily empirical, and consequently uniformity of procedure is important. Recognising this, the Institute of Brewing has appointed Committees to draft and amend instructions for malt analysis.¹

1. Extract.

50 g. of malt is weighed out, one additional corn being added to allow for loss in grinding. The malt is ground in a Seck laboratory mill set at any determinate degree, and the grist so obtained should weigh 50 ± 0.03 g. The Malt Analysis Committee of the Institute of Brewing in 1906 recommended that for general purposes the Seck mill should be set at 25 on the arbitrary scale provided. Later, however, it was found that the scales of different mills were not alike, but the Committee, having examined many mills, found that when the rolls were set at 25, the average distance between them was about 0.5 mm. They therefore suggested that for general purposes the rolls should be set at 0.5 mm. apart, measured by a feeler gauge. The grist is transferred to a glass beaker of about 600 c.c. capacity; copper beakers, if kept scrupulously clean and used daily, are permissible, but in other circumstances their use may give rise to error.² About 360 c.c. of water at 155° F. (68.3 C.) is poured on to the grist, the mixture being well stirred to prevent balling. The beaker is covered with a clock-glass and placed in a water-bath at such a temperature that the contents of the beaker are kept at exactly 150° F. (65.6 C.) for one hour. The mash is stirred at intervals of about ten minutes. The Committee recommend maintaining the above-mentioned temperature (150° F.) for fifty-five minutes and subsequently raising it to 158° F. (70° C.) in five minutes. This, however, in our experience, is unnecessary

¹ *J. Inst. Brewing*, 1906, 2, 1; 1910, 16, 529.

² Cf. A. R. Ling and G. M'Laren, *J. Inst. Brewing*, 1908, 14, 160.

and tends to give higher results only with exceptionally steely malts. The mash is next cooled by immersing the beaker in running water, and when at 60° F. (15°·6 C.) is transferred to a measuring flask and made up to 515 c.c. The reason for choosing a volume of 515 c.c. is that it is assumed that the grains from 50 g. of malt occupy on an average a volume of 15 c.c. Apart from the fact that thin malts from six-rowed barleys give more grains than do malts from two-rowed barleys, this volume is more than should be allowed for the average malt. According to one of the author's measurements the average value is about 12 c.c. No sensible error is introduced if the temperature is within 5° of 60° F. when the volume is adjusted. The contents of the flask are shaken and filtered through a large-ribbed paper. (Schleicher and Schüll's No. 595, 24 cm., serves well.) The first 50 c.c. of the filtrate is rejected, after which about 100 c.c. is collected for the determination of specific gravity and tint. The specific gravity can be determined with sufficient accuracy by the use of a 50 c.c. specific gravity bottle with perforated stopper, weighing to the nearest milligram. The excess specific gravity at 60°/60° F. (water = 1000) multiplied by 3·36 gives the extract of the malt in brewers' lb. per quarter of 336 lb.

Specific gravities cannot always be taken at 60°/60° F.; it may be impossible to cool the solution sufficiently, and, even if possible, this may lead to the deposition of dew on the bottle. In such circumstances it is best to make the determination at t°/t° , where t° is a temperature not far removed from that of the laboratory, and to correct the extract thus found for the difference in the coefficients of expansion of water and 10 lb. malt worts (that is, of solutions having a specific gravity of 1028 or thereabouts, such as are yielded by ordinary malts in this process). The correction¹ to be applied is as follows:—

$$E_{60^\circ} = E_{t^\circ} + (t - 60) 0.06,$$

where E_{t° represents the extract calculated from the observed specific gravity at t°/t° and E_{60° the true extract which would have been found had the determination been made at 60°/60° F. It will be observed that the correction is so small that the use of a thermometer inaccurate to the extent of 1° will not influence the result seriously, provided the same thermometer be used for determining the temperature of the extract and of the distilled water, which temperatures should agree as closely as possible, a difference of 1° F. introducing an error of 0.3 lb. The water-content of the specific gravity bottle should be checked daily.

¹ The correction given here, which differs slightly from that first suggested by one of us (*J. Inst. Brewing*, 1908, 14, 12), is based on experimental work by F. E. Day and S. L. Amos (*J. Inst. Brewing*, 1914, 20, 196).

2. Tint.

In the case of pale and amber malts, the bright extract obtained as above described is placed in a 1-in. cell of a Lovibond tintometer, and its tint recorded in colour units of the series "52" glasses. The wort must be quite bright, but refiltration in presence of kieselguhr is not permissible. Filtration through a sufficient bed of grains contained in an unribbed filter seldom fails to give a brilliant wort. The tintometer is best directed against a piece of thin, white tissue paper attached to a north window, some 2-3 ft. distant from the tintometer.¹ The experiment must not be carried out in direct sunlight.

3. Moisture.

About 5 g. of malt is ground and transferred to a broad, short weighing-bottle of which the tare is known. The stopper is inserted, the bottle and its contents weighed to the nearest mg., and the bottle then placed (with its stopper on its side across the mouth of the bottle) in a vigorously boiling and well-ventilated water-oven. After five hours, the bottle is transferred to a desiccator, allowed to cool, and weighed. It is important that during the five hours that the malt remains in the water-oven, the door should not be opened.

4. Diastatic Power.

Since no enzyme has yet been isolated in a pure condition—in fact it is not even known that an enzyme consists of a single substance—the estimation of the quantity present in a given product is not possible. In the case of malt diastase, however, the comparative starch converting power of malts under standard conditions can be measured, whereby a value is obtained which is designated the diastatic power. This is effected by measuring the cupric reducing power of a solution of soluble starch which has been partially converted by a known mass of a malt. It is necessary that the starch conversion be carried so far only that the cupric reducing power of the dissolved matter in the converted liquid shall not be higher than corresponds with the production of 35-40 per cent. of maltose. Up to this point the reaction proceeds as a linear function of the time or mass. Subsequently it becomes a logarithmic function. The discovery of this so-called law of proportionality is due to Kjeldahl.²

This law is as follows:—The relation between the diastatic powers of two or more malts may be expressed by the cupric reducing powers which their conversion products exhibit when equal masses act on a solution of soluble starch for the same time and at the same tempera-

¹ J. L. Baker and H. F. E. Hulton, *J. Inst. Brewing*, 1906, 12, 302; 1907, 13, 26.

² *Comptes rend. Carlsberg*, 1879, 1, 109.

ture, provided the cupric reducing power calculated on the solid matters of the conversion products does not exceed a value of 35-40 per cent. expressed as maltose.

It is somewhat unfortunate that this law has been ignored by certain chemists who have formulated methods for the determination of the diastatic power of malt or of malt extract. Thus one of the writers¹ had occasion to point out that the method proposed by E. F. Harrison and D. Gair² cannot give accurate results, inasmuch as it does not take into account Kjeldahl's law of proportionality.

The determination of the diastatic power of malt is now carried out by a method devised by C. J. Lintner,³ the conditions of which include those required by Kjeldahl's law of proportionality.

25 g. of finely ground malt is digested with 500 c.c. of water at 60°-70° F. (15°-21° C.) for three hours. No error is introduced by prolonging the period of digestion by an hour, whereas reducing it may lead to an appreciably lower result. The extract is then filtered. A solution of soluble starch (see p. 814) containing 2 g. in 100 c.c., is prepared, and a volume of 10 c.c. of this solution is placed into each of ten test tubes. Subsequently an increasing quantity of the bright malt extract is placed into each of the test tubes, the first receiving 0.1 c.c., the second 0.2 c.c., the third 0.3 c.c., and so on. The contents of the tubes are mixed by shaking, and kept at 70° F. (21° C.) for an hour.⁴ 5 c.c. of Fehling's solution is then added to each, and after mixing the contents of the tubes, they are placed in a bath of boiling water for ten minutes, ebullition being maintained during this time. The tubes are now taken out of the bath, placed in order and examined, when it will be found that unreduced Fehling's solution is present in some, usually towards the end of the series. The point of exact reduction will lie between the first tube of the series, which exhibits a blue colour, and the adjacent tube on the left. In order to obtain a more accurate measurement, a second experiment may be carried out with a series of tubes to which quantities of malt extract are added between the limits indicated by the preliminary experiment, the volumes of malt extract differing only by 0.02 c.c.

The diastatic power of a malt is taken as 100 when 0.1 c.c. of standard malt extract produces sufficient reducing sugar to reduce 5 c.c. of Fehling's solution completely.

There are certain disadvantages attending this method, and a much more expeditious and convenient modification of it has been devised by one of the authors.⁵ The method was adopted as the standard method

¹ *Chem. and Drug.*, 1910, 76, 52.

² *Pharm. J.*, 1906, 77, 94; 1909, 82, 388.

³ *Z. ges. Brauw.*, 1885, 8, 281.

⁴ The temperature originally suggested by Lintner was 17°.

⁵ A. R. Ling, *J. Inst. Brewing*, 1900, 6, 355.

for the purpose by the Malt Analysis Committee of the Institute of Brewing.¹ As now used, it is carried out as follows:—

The malt is extracted in the same manner as for the Lintner method. A known volume—usually 3 c.c. for brewery malts, or a lesser volume for distillery and other highly diastatic malts—is allowed to act on 100 c.c. of 2 per cent. soluble starch solution (see p. 814) at 70° F. (21° C.) for an hour in a 200 c.c. flask. An error here of 1° F. or two minutes will introduce an error of about 3 per cent. 10 c.c. of *N*/10 sodium hydroxide is then added in order to stop further diastatic action, the liquid made up to 200 c.c. with distilled water, well shaken and titrated against 5 c.c. portions of Fehling's solution, using ferrous thiocyanate as indicator (see section on "Sugar," this Vol., p. 564). The results are calculated by the following formula:—

$$D = \frac{1000}{xy}$$

in which *D* equals the diastatic power of the malt, *x* equals the number of cubic centimetres of malt extract contained in 100 c.c. of the fully diluted starch conversion liquid, and *y* equals the number of cubic centimetres of the conversion liquid required for the reduction of 5 c.c. of Fehling's solution.

The diastatic power of concentrated malt extracts may also be determined by this method, the results being corrected in this case for the reducing power of the extract itself, which may be greater than that of the products of its action on starch for one hour at 70° F. In determining the diastatic power of malts, it is customary to neglect the reducing power of the cold water malt extract, which is so small that it causes the diastatic power to be over-estimated by only about 1° Lintner.

The diastatic power of a malt determined in the above manner (Lintner value) is of very little direct value to the brewer in guiding him as to how the starch conversion will proceed in the mash tun. The rotatory and reducing powers of worts from malts mashed at one and the same temperature are, however, influenced by the Lintner value of the malt, and generally, as might be expected, it may be said that the higher the Lintner value, the lower the rotatory power and the higher the reducing power of the wort. The influence is, however, a small one, and is never proportional to the Lintner scale, whilst in certain cases the results are anomalous.² The chief use of the Lintner value is in indicating whether the malt itself has been made up on correct lines at the malting. There should be a relation between the Lintner value and the tint of the malt. Here, however, the relation is subject to variation from season to season. In some seasons, for example, an amber malt having a tint of 20 Lovibond will

¹ Cf. A. R. Ling, *J. Inst. Brewing*, 1906, 12, 1.

² *Ibid.*, 1911, 17, 581.

show a Lintner value of 8-10, whilst in others a malt of the same tint would have a Lintner value of 15 and above. Nor is the relation of these two values identical for all barleys of one and the same season. It is influenced largely by the kind of barley and the district in which it was grown.

Preparation of Soluble Starch for the above Test.—Prime farina or potato starch is digested with hydrochloric acid of sp. gr. 1.037 at 60°-65° F. (15°-18° C.) for seven days, the mixture being stirred daily. The operation is conveniently carried out in Winchester quart bottles, 1 lb. of starch and 1000 c.c. of diluted acid being suitable quantities for each such bottle. The soluble starch is washed very thoroughly by decantation, at first with tap water, and later on with distilled water, until the wash water is free from chlorides. It is collected on a filter paper, placed in a Buchner's funnel, dried as completely as possible on the pump, and then spread out on a new unglazed porous plate. The starch should be dried at a gentle heat (110° F.) as quickly as possible. When dry, the starch is triturated in a porcelain mortar and rubbed through a fine hair sieve. Care should be taken that the soluble starch is not alkaline, nor should it be acid beyond a certain degree. The limit of acidity of soluble starch adopted in the writers' laboratories is that 200 c.c. of a 2 per cent. solution titrated hot against $N/10$ alkali shall not require more than 0.2 c.c. of $N/10$ alkali for neutralisation when alizarin is used as indicator.¹

5. Cold Water Extract.

25 g. of ground malt is digested with 250 c.c. of very dilute ammonia (made by diluting 20 c.c. of $N/10$ ammonia to 250 c.c. with distilled water) for three hours at 70° F. (21° C.), stirring about three or four times during this period. After filtering, the specific gravity of the filtrate is taken at 60° F. (15°-6 C.), compared with water at the same temperature. The excess specific gravity over water (= 1000) divided by 3.86 and multiplied by 10 gives the percentage of cold water extract.

The authors attach very little importance to this test, but as some people regard with disfavour a malt giving a cold water extract in excess of some assigned amount, it is important that the determination, if made at all, should be made under rigidly standardised conditions, as the results are profoundly modified by small variations in procedure. The use of dilute ammonia in place of water, which was formerly used, prevents the action of diastase almost entirely, but the results depend largely on the way the filtration is conducted. If the whole contents of the beaker be thrown on to a 24 cm. filter, the first 50 c.c. of the filtrate rejected and the remainder (about 100 c.c.) collected for the specific gravity determination, results may be duplicated within 0.1

¹ Cf. *J. Inst. Brewing*, 1908, 14, 19.

per cent. A brilliant filtrate is seldom obtained, and any attempt to secure one by putting the cloudy liquid through the filter a second time may easily lead to the extraction of an additional 1 per cent. of solids.

6. Modification.

In order to obtain some quantitative expression of the degree of modification of a malt, the extract yielded by the method already described may be compared with that yielded by a portion more or less finely ground. The most convenient comparison is made between malt ground at 25 and 40 Seck, though sometimes more valuable information is obtained by making one determination on very finely ground malt. A well-modified malt will yield practically the same extract in each experiment, whereas with a badly modified one the results may differ by several pounds.

7. "Saccharification" Time.

This test measures the time at which the starch disappears when a malt is mashed. To some extent it is a measure of the diastatic power of a malt, but its indications are chiefly of value in showing whether or not a malt is well modified. Tender malts invariably "saccharify" more rapidly than vitreous malts. In this connection, however, it may be pointed out that better and more reliable results may be obtained by the expert by physical examination. The test is carried out as follows:—

10 g. of malt, ground at 25 Seck, is mashed with 100 c.c. of water at 155° F. (68°·3 C.), and the mixture kept at 150° F. (65°·6 C.), in a water-bath with frequent stirring. After fifteen minutes, a portion is withdrawn and tested with iodine. If starch is shown to be present, the experiment is continued, and portions of the wort are withdrawn at five-minute intervals and tested. When the starch reaction is no longer given, the time from the commencement of the experiment is noted and returned as the Saccharification Time. In the case of some steely malts, this may exceed thirty minutes.

8. Nitrogen.

Total nitrogen may be determined by Kjeldahl's method on 3 g. of the malt, which need not be ground.

9. Soluble Uncoagulable Albuminoids.

In England, specifications for malt more often set a limit to this number than to that of total nitrogen. For its determination, 200 c.c. of the cold extract prepared for the determination of diastatic power is boiled in a beaker for twenty minutes or until reduced to less than 100 c.c. in bulk. The solution is cooled, transferred to a 100 c.c. measuring flask, made up to the mark, shaken and filtered. The nitrogen in 20 c.c. of the filtrate (= 2 g. of malt) is then determined by

Kjeldahl's method, the percentage of nitrogen found is multiplied by 6.3, and the result returned as the percentage of soluble uncoagulable albuminoids. The soluble uncoagulable nitrogenous matters thus determined are in part at least of much simpler constitution than the true proteins, and their nitrogen-content differs notably from the 16 per cent. implied by the use of the factor 6.3. The above method of stating the results, however, has become conventional, perhaps because the number actually found—the percentage of soluble uncoagulable nitrogen—is a very small number, of the order of 0.3.

10. Physical Examination.

The chemical analysis of malt is always supplemented by a "hand examination," which, even alone, gives the expert much information. No written directions can take the place of experience in this matter. The expert can judge the moisture-content and degree of modification by "biting" malt, and the degree of curing by the flavour. No special skill is required to detect stones, foreign seeds or mouldy or badly damaged corns, but the enumeration of "damaged" corns is best not attempted. Well-made malt has a mealy appearance when cut in half. Imperfectly modified malt when cut, preferably longitudinally, has a more or less vitreous appearance, which may extend throughout the corn or be confined to the distal end. Even well-modified malt may be rendered steely by mismanagement on the kiln. The only numbers derived from the physical examination of malt that ever find their way to a certificate of analysis are numbers relating to the growth of the acrospire and, less frequently, numbers derived from a test known as the "Sinker" test. This latter test, which in its simplest form consists in stirring 100 corns with water for a few seconds and counting those that sink at once, is capable of giving useful information to the expert, who is guided as much by the behaviour of the non-sinkers as by the number of sinkers; but as a quantitative test it is too dependent on undefined experimental conditions for the results to be of value to anyone but the maker of the test.

Growth of Acrospire.—Analytical reports frequently, but not always, include a quantitative statement of the growth of the acrospire. 100 corns or more are counted out and arranged in groups according to the length to which the acrospire has grown, expressed as a ratio of the whole length of the corn; for example:—

Still corns, in which no visible acrospire development has taken place,			
$\frac{1}{2}$	grown corns, in which the spire extends	$\frac{1}{2}$	the length of the grain,
$\frac{2}{3}$	"	"	"
$\frac{3}{4}$	"	"	"
Fully	"	"	has just reached the end of the grain,
Grown-out corns	"	"	exceeds the length of the grain.

Usually most of the corns will fall into two adjacent classes. If $\frac{3}{4}$ to fully grown, the sample would be described as fully grown; if $\frac{2}{3}$ to $\frac{3}{4}$, as well grown. A sample with 40 per cent. or more of $\frac{1}{2}$ grown corns would be described as short-grown, but not necessarily as under-grown.

Results of Analysis.

Extracts range from below 80 lbs. to nearly 100 lbs. per quarter (rarely more). English malts and malts made from the finer varieties of foreign barley more often than not give extracts in excess of 95 lbs., but in some seasons this would be a good, in others only a moderate yield. The lower extracts are given by malts made from light, husky foreign barleys from the Pacific slopes of the United States, from Asia Minor, North Africa, and India, though the barleys imported from India are improving very rapidly.

Tints range from 3-5 for pale malts to 20 or more for amber malts.

Diastatic powers vary from 30-45 for pale malts to 15 or less for amber malts.

The percentage of moisture is usually less than 3 per cent., in fact many brewers refuse to accept malt containing more. When freshly made, the moisture-content may be below 1 per cent.

Cold extracts range mostly from 15 to 20 per cent., the lower percentage rarely being found except in light foreign malt, the higher being above the average for English and the finer foreign varieties.

Results are returned to the first place of decimals, except in the case of diastatic power, which is returned to the nearest integer only.

BROWN AND CRYSTAL MALTS.

These materials, as well as black malts, require special methods of analysis, owing to their lack of diastatic power and their high colour.

1. Extract.—50 g. is ground in a Seck mill so set that there is a distance of 0.5 mm. between the rolls (see p. 809), and the grist is mashed with 300 c.c. of distilled water at 158° F. (70° C.) and 100 c.c. of cold water malt extract previously heated to 150° F. (65.6° C.). The cold water malt extract is made by digesting ground malt of 30°-40° Lintner with three times its weight of distilled water for an hour at 60°-70° F. (15.6-21° C.) and subsequent filtration. The mash is kept for one hour at a temperature of 150° F., then cooled to 60° F., made up to 515 c.c., shaken, filtered, and the specific gravity taken. Simultaneously with the above experiment, 100 c.c. of the malt extract diluted with 300 c.c. of water is kept at 150° F. for one hour. Subsequently it is cooled to 60° F., made up to 500 c.c., filtered, and its specific gravity taken. The difference between the specific gravities of the filtrates in the two experiments (water = 1000) multiplied by 3.36 gives the extract

per standard quarter of 336 lbs. Brown and crystal malts, like black malts, are not commonly purchased on the basis of the standard quarter of 336 lbs., but the results of analysis are most conveniently expressed in this way.

2. Tint.—20 c.c. of the above extract, which must be brilliant, is diluted to 100 c.c. and the colour read in a 1-in. cell, using a Lovibond tintometer and glasses of the "52" series.

Brown malts give extracts ranging from 80 to 90 lbs. per 336 lbs., and possess a tint which usually exceeds 20 when determined as described.

BLACK BARLEYS AND MALTS.

1. Extract.—A little over 50 g. is finely ground in a coffee mill, and of this exactly 50 g. is extracted with 350 c.c. of boiling distilled water, care being taken to avoid balling. The vessel containing the mash is kept in a boiling water-bath for one hour, after which its contents are cooled, made up to 515 c.c. at 60° F. (15°·6 C.), shaken, filtered through an open-textured filter, and the specific gravity of the filtrate is determined. From the specific gravity of the filtrate, the extract per quarter of 336 lbs. is calculated exactly as for ordinary malts, although the basis of purchase is not usually the standard quarter of 336 lbs.

2. Tint.—20 c.c. of the above extract, which must be brilliant, is diluted to 1000 c.c. and the colour read in a 1-in. cell, using a Lovibond tintometer and glasses of the "52" series.

The extract of black barleys and malts is usually a little over 90 lbs. per 336 lbs. and the tint of the order of 30.

C.—CARMEL.

1. Extract.—10 g. is dissolved in distilled water, and the solution made up to 100 c.c. at 60° F. (15°·6 C.), and filtered. The specific gravity of the filtrate is determined, and the excess over water (=1000) multiplied by 2·24 gives the brewers' extract in lbs. per 224 lbs.

2. Tint.—10 c.c. of the above extract is diluted to 1000 c.c., and the colour is read in a 1-in. cell, using a Lovibond tintometer and glasses of the "52" series.

3. Ash.—3 g. is weighed into a silica (or porcelain) dish, treated with 2 c.c. of concentrated sulphuric acid, and the dish heated over a flame until intumescence is complete. It is then placed in a muffle at a low red heat. It is customary to deduct one-tenth from the weight of the sulphated ash.

4. Iron.—More than a minute trace of iron is objected to in brewing materials, and as caramel is often manufactured in iron vessels by a process which tends to attack the iron, the ash should always be dissolved in acid, and iron determined colorimetrically with thiocyanate.

5. Deportment with Beer.—Caramel when dissolved in beer should

not give rise to any sediment. The most stringent test is made by the use of pale bitter ale. A direct test is made and, if this is prolonged beyond twenty-four hours, some of the beer without caramel should be tested at the same time as a control.

Caramel of good quality approximates 40 in colour and yields an extract of 65 lbs. or not much less.

D.—FLAKED MAIZE AND RICE.

Flaked materials are usually examined for extract, moisture, and oil-content. A starch determination is sometimes made, but as these materials command a relatively high price because their starch is supposed to have been rendered amenable to diastase, they are properly judged by the extract they yield when mashed with pale malt or malt extract, any starch not converted in this test being useless to the brewer who introduces such materials direct into his tun.

1. Extract.—This may be determined as described under Brown and Crystal Malts (p. 817). An alternative method, yielding results several pounds lower, but more nearly representing the extracts obtainable in practice, is the following :—25 g. of flakes and 25 g. of pale malt, of known extract and with a diastatic power closely approximating but not exceeding 30°, are mashed together, as described under Malt (p. 809). The extract of the mixed grist per quarter of 336 lbs. is calculated in the usual manner. Twice this extract, less the known extract of the malt used, gives the extract of the flakes per quarter of 336 lbs.

2. Moisture is determined as in malt.

3. Oil is determined by extracting the finely divided flakes with ether in a Soxhlet or other continuous extractor.

Extracts approximate 100 lbs. and are often higher, moisture percentages range from 6 to 12 per cent. or more, whilst the percentage of oil approximates 1 in the case of maize and 0.3 in rice, rarely exceeding these amounts by more than 0.1 per cent.

E.—GRITS AND RAW GRAIN.

The value of these materials to the brewer is very fairly gauged from their starch-content. This is best estimated by one or other modification of Lintner's polarimetric method (see section on "Starch and Dextrin," this Vol., p. 667).

In grits it is usual to estimate the percentage of oil, large proportions of oil being objectionable.

The percentage of starch in maize grits with 10 per cent. of moisture averages nearly 75, that of rice grits of equal moisture-content nearly 80. With moisture percentages of 14, which are not very uncommon,

the starch-content is correspondingly less. The content of oil approximates, but is usually less than 1 per cent.

F.—BARLEY.

Barley is not only the principal raw material of the brewing industry as the raw material of malt, but is also used to some extent unmalted, displacing maize and rice grits or flakes.

When supplied as flaked material, it is best valued from the extract yielded when mashed with pale malt, as described under Flaked Maize (p. 819).

If intended to be treated with other starchy materials in a converter, it may be more accurately valued from its content of starch (see below).

Barley for malting purposes is almost invariably purchased on the basis of hand examination. Frequently, however, the chemist is asked to determine moisture and total nitrogen and, since reasonably accurate and speedy means have been devised for the purpose, to estimate starch. The starch percentage alone would serve to value the barley if a high percentage of extract were the only thing valued in malt. The yield of malt in lbs. per quarter of barley will be more or less according as the moisture in the barley is low or high, but the lbs. of brewers' extract obtainable from 1 quarter of barley is very fairly measured by the starch-content of the barley. However, malt is not valued solely on its yield of extract, nor malting barley on its starch-content, though this is an important factor.

So far as chemical analysis can supply any measure of the brewing "quality" of barley, as distinguished from its capacity to yield extract, the nitrogen-content, expressed as a percentage on the moisture-free barley, is probably the most useful figure. In general, the lower the nitrogen-content, the more highly will the barley and the malt made from it be prized. No limits of nitrogen-content can be given here, as any limits must necessarily vary for barleys of different type and origin.

Since the protein substances in barley and malt contribute a negligible proportion of the extract (in a quantitative sense—the proteins and their cleavage products in wort fulfilling important functions, though small in amount), and since moisture is wholly useless, barley of any one type may be very fairly valued as a result of the estimation of moisture and nitrogen, without further determinations. The nitrogen-content is a guide to the brewing quality of the barley, and the content of nitrogenous substances ($N \times 6.3$) and of moisture are data from which the extract yield can be predicted with fair accuracy by an expert. For the constituents of barley, apart from starch, moisture and protein, are fairly constant in amount for any one type of barley. Partly because so much may be learned from these two determinations

alone, and partly because the estimation of starch in barley was until recently a very tedious operation, the estimation of moisture and nitrogen are much more often required of the analyst than the estimation of starch.

1. **Moisture.**—This is determined as in malt.

2. **Nitrogen.**—This is determined as in malt.

3. **Starch.**—For this purpose E. Ewers' method¹ is convenient. It is carried out as follows:—5 g. of the finely ground barley is washed into a dry flask with 50 c.c. of dilute hydrochloric acid containing exactly 1.124 per cent. of HCl. The mixture is heated for exactly fifteen minutes in boiling water, cooled rapidly, and washed into a 100 c.c. flask. 10 c.c. of a 4 per cent. solution of phosphotungstic acid and 2-3 c.c. of alumina cream are added, and the whole made up to 100 c.c. and filtered. The filtrate is read in a polarimeter in a 200 mm. tube. The reading (corrected for the blank, see below) in degrees Ventzke, multiplied by 1.912, gives the percentage of starch in the sample. A blank experiment must be made under the same conditions, except that 50 c.c. of *N*/50 sodium hydroxide is substituted for the 50 c.c. of hydrochloric acid.

4. **Weight of Skins** (Glumes or Paleæ).—This determination is seldom made in this country, but the following method, due to Luff,² has been found very useful as an aid to the estimation of probable extract yield, more especially in the years preceding the formulation of Lintner's method for the direct determination of starch.

About 50 corns (2 g.) are weighed exactly, covered with 10 c.c. of 5 per cent. ammonia in a stout flask, which is corked and kept in a water-bath at 80° for one hour. The paleæ can then be readily removed, and are transferred to a tared weighing-bottle, dried in a steam-oven, and weighed. Luff dried at 105° and added one-twelfth to the weight found, to correct for loss of solid substance from the paleæ by the solvent action of ammonia. His experiments showed that this gave a closer approximation to the original weight of the paleæ, but the uncorrected figure is quite as useful for estimating extract indirectly from the percentages of protein, moisture, and paleæ by reference to direct malting experiments. One-twelfth of the weight of the paleæ is less than 1 per cent. on the barley.

The Physical Examination of barley, on which it is almost exclusively bought and sold, is an unprofitable subject for a written essay without demonstration, and its discussion would be quite out of place here. One test, other than the chemical tests, however, must be referred to briefly.

5. **Germination Test.**—It is fairly frequently required to report on the germinative "energy" and germinative "capacity" of samples of

¹ *Z. ges. Brauw.*, 1908, 31, 378.

² *Ibid.*, 1898, 21, 485.

barley. The former of these expressions is generally used to denote the percentage of corns that show visible signs of growth within three days when placed under favourable conditions, whilst germinative "capacity" usually means the percentage that show signs of growth when the period of incubation is prolonged to five days or more. The results depend very much on the apparatus and other conditions, and the type of apparatus used as well as the temperature should always be recorded. The apparatus most in use is that of Coldewe. It consists of a glass vessel with a constriction about $1\frac{1}{2}$ inches from the top, on which rests a porcelain plate provided with a hundred perforations, into each of which a corn of barley is inserted with the germ end downwards. The glass vessel is filled to about $\frac{3}{4}$ of its content with water, the porcelain plate placed on the constricted portion, the corns covered with moist sand, and a wooden cover, the underside of which is covered with a layer of felt, placed over the sand. A small thermometer attached to the cover serves to indicate the temperature at which the experiment is being conducted. Two or three more elaborate appliances, for the treatment of numerous samples simultaneously, have been described and possess certain advantages, but nothing, in the authors' opinion, can compare with a muslin bag, containing a counted number of corns, which are steeped for twenty-four hours or longer, and then buried in a piece of growing malt in a maltings. The surrounding grain, kept always by the maltster within the temperature limits proper to malting, forms an ideal thermostat and regulator of humidity and aeration. Failing the neighbourhood of maltings or Coldewe's or other apparatus, barley may be steeped for twenty-four hours and kept between pieces of wet flannel or filter paper in a cool place (10° - 15°).

The starch-content of barley approximates 50 per cent., the protein-content ($N \times 6.3$) 10 per cent., whilst the moisture varies from 8 to 20 or more per cent., the average for British barley being perhaps 15 per cent.

G.—RAW CANE SUGAR.

Raw and partially refined cane sugars are usually valued by their polarisation (see section on "Sugar," this Vol., pp. 645 *et seq.*), although this does not represent accurately the percentage of sucrose, since they invariably contain reducing sugars for which the polarisation cannot be corrected, as the rotatory power of the reducing sugars is unknown. The most accurate means of estimating sucrose in these products is by the method of double polarisation (Clerget's method), or from the reducing power before and after heating with dilute acid (*loc. cit.*).

Brewers use cane products of widely varying purity, ranging from sugar candy, polarising 98-99 per cent., to dark coloured, flavoury

products, polarising only 75 per cent. with 15 per cent. of reducing sugars, and sometimes as much as 5 per cent. of ash.

The luscious secondary matters in raw cane products have a distinct value to the brewer. The impurities of raw or partially refined beet sugar, on the other hand, are so objectionable that no brewer would knowingly use such sugars, nor could he well fail to detect them if delivered in substitution for cane products. Admixture of raw beet sugars with a flavoury cane sugar, however, masks to some extent the characteristics on which the brewer relies for his guidance, and reference may be made to a paper by Ling,¹ in which it is shown that raw beet sugars contain a much larger proportion of nitrogenous matters than do raw cane sugars.

H.—INVERT SUGAR.

Invert sugar for use by brewers is prepared by hydrolysing raw or partially refined cane sugar, since highly refined cane sugar lacks the luscious secondary products which give character to the invert and to beers made from it. Commercial invert therefore contains not only dextrose, lævulose, uninverted sucrose and water, but ash constituents, nitrogenous substances, and unfermentable carbohydrates. As the unfermentable substances may be optically active and possess cupric reducing power, and as dextrose and lævulose may be present in variable proportions (the former always predominating), the analysis of commercial invert sugar is somewhat complicated.

The first practicable scheme for the analysis of invert sugar was that worked out by G. H. Morris.² The following method, made possible by improvements in the volumetric estimation of reducing sugars, follows the same general principles as that of Morris, and is simpler than his method.

1. Albuminoids.

Nitrogen is determined by Kjeldahl's method, and the result multiplied by 6.3 and returned as albuminoids.

2. Ash.

This is determined as described under Caramel (p. 818), the method, including the deduction of one-tenth from the weight of the sulphated ash, being in almost universal use in the analysis of sugars. As the ash constituents of artificial invert sugar are usually present in large part as sulphates, the correction is probably too large, but the convention is established and the error involved is not important.

¹ *J. Inst. Brewing*, 1914, 20, 185.

² *Ibid.*, 1898, 4, 162.

3. Brewers' Extract and Water.

25 g. is dissolved in water, the solution made up to 250 c.c., filtered, and the specific gravity of the filtrate determined.

Brewers' Extract.—The excess specific gravity of the above filtrate (water = 1000) multiplied by 2.24 gives the brewers' extract in lbs. per 224 lbs.

Water.—This is calculated on the assumption that the other organic solids have the same "solution factor" as pure invert sugar, and that the ash constituents have a "solution factor" twice as high. This is only approximately true, but the minor constituents are present in small quantity, and pure invert sugar in approximately 8 per cent. solution can be estimated with very small error by dividing the excess gravity (water = 1000) by 3.88, which is spoken of as the "solution factor" of invert sugar in a concentration of 7-8 per cent. The solution factor of the ash constituents varies somewhat but approximates 8, and is usually assumed to be twice that of invert sugar.

The solid matter in the invert is therefore calculated by dividing the excess gravity of the 10 per cent. solution by 0.388 and deducting the percentage of ash already found. The difference between 100 and the number so found is the percentage of water.

4. Sucrose, Dextrose, and Lævulose.

These are estimated in the following manner, making use of the Table on p. 825. In addition to the directions for making the analysis, the figures obtained in a particular case are added to exemplify the calculation of results.

The 10 per cent. solution made for the estimation of brewers' extract is observed in a 200 mm. tube in a Ventzke-Scheibler half-shadow polarimeter. 10 c.c. of the 10 per cent. solution is diluted to 500 c.c. and titrated against 10 c.c. of Fehling's solution.¹

In a particular case a commercial invert sugar gave a reading in 10 per cent. solution in a 200 mm. tube of -4.7 divisions, and 10 c.c. of Fehling's solution required 36.45 c.c. of 0.2 per cent. solution, corresponding to a percentage of apparent invert sugar of 0.1441 (see Table, col. I).

Another portion of 10 c.c. of the 10 per cent. solution is diluted with 100 c.c. of water and 20 c.c. of $N/2$ hydrochloric acid. The mixture is raised to a boiling temperature and maintained in ebullition for one minute, after which it is cooled, neutralised by the addition of 20 c.c. of $N/2$ sodium hydroxide, and made up to 500 c.c. The solution is then titrated against 10 c.c. of Fehling's solution.

¹ The method adopted is that of Ling and Rendle, *Analyst*, 1905, 30, 183; 1908, 33, 170; Ling and Jones, *ibid.*, 1908, 33, 160; see section on "Sugar," p. 564.

In the case cited, after hydrolysis with acid, only 35.95 c.c. of 0.2 per cent. solution were required to reduce 10 c.c. of Fehling's solution. By reference to the Table, it will be seen that this corresponds to a percentage of apparent invert sugar of 0.1460, whereas before inversion the percentage of apparent invert sugar was only 0.1441. The difference, 0.0019 per cent. is the measure of the sucrose originally present, in terms of invert sugar, and the percentage of *sucrose* in the sample is accordingly $0.0019 \times 0.95 \times 500 = 0.9$ per cent.

Table 61.

Reducing Values for Dextrose, Lævulose, Invert Sugar, and Maltose. (Ling and Jones.)

Volume of solution required by 10 c.c. Fehling's solution.	Dextrose.		Lævulose.		Invert sugar.		Maltose.	
	D. Dextrose in 100 c.c. of solution.	D'. Fehling's solution equivalent to 1 g. dextrose.	L. Lævulose in 100 c.c. of solution.	L'. Fehling's solution equivalent to 1 g. lævulose.	I. Invert in 100 c.c. of solution.	I'. Fehling's solution equivalent to 1 g. invert.	M. Maltose in 100 c.c. of solution.	M'. Fehling's solution equivalent to 1 g. maltose.
c.c.	g.	c.c.	g.	c.c.	g.	c.c.	g.	c.c.
20	0.2427	206.0
21	0.2332	205.1	0.2412	197.5	0.3888	122.5
22	0.2226	204.2	0.2411	188.5	0.2311	196.8	0.3711	
23	0.2138	203.4	0.2312	188.0	0.2218	196.0	0.3550	
24	0.2056	202.6	0.2222	187.5	0.2132	195.5	0.3402	
25	0.1981	201.9	0.2138	187.1	0.2052	194.9	0.3266	
26	0.1911	201.3	0.2060	186.7	0.1980	194.3	0.3140	
27	0.1846	200.7	0.1988	186.3	0.1910	193.9	0.3023	
28	0.1784	200.1	0.1921	186.0	0.1846	193.4	0.2915	
29	0.1728	199.6	0.1857	185.6	0.1787	193.0	0.2815	
30	0.1675	199.1	0.1798	185.4	0.1731	192.5	0.2721	
31	0.1625	198.6	0.1743	185.1	0.1678	192.2	0.2633	
32	0.1577	198.2	0.1691	184.8	0.1629	191.8	0.2551	
33	0.1532	197.8	0.1642	184.6	0.1583	191.5	0.2474	
34	0.1490	197.4	0.1596	184.3	0.1539	191.2	0.2401	
35	0.1450	197.0	0.1552	184.1	0.1497	190.9	0.2332	
36	0.1412	196.7	0.1511	183.9	0.1458	190.6	0.2268	
37	0.1377	196.4	0.1472	183.6	0.1421	190.3	0.2206	
38	0.1343	196.0	0.1435	183.4	0.1385	190.1	0.2148	
39	0.1310	195.8	0.1399	183.3	0.1349	189.8	0.2093	
40	0.1279	195.5	0.1366	183.1	0.1319	189.6	0.2041	122.5
41	0.1334	182.9	0.1288	189.4
42	0.1298	182.8	0.1259	189.2
43	0.1274	182.6

Before the dextrose and lævulose can be calculated from the rotation (corrected for that due to sucrose) and the reducing power of the original sample, the rotation and reducing power due to unfermentable substances must also be known. To this end, 25 g. of the sample is dissolved in 200 c.c. of water in an Erlenmeyer flask and the solution is sterilised by boiling. About 5 c.c. of yeast decoction (1:5) and 3 g. of washed pressed yeast are added to the cooled solution, and the flask

is plugged with cotton wool and maintained at about 70° F. (21° C.) for three to four days. The mixture is then transferred to a 250 c.c. flask, a little alumina cream is added, the volume adjusted to 250 c.c., and the contents of the flask mixed and filtered. The filtrate is observed in a 200 mm. tube in a Ventzke polarimeter, and another portion is transferred to a burette and titrated against 10 c.c. of Fehling's solution.

In the case cited, a 10 per cent. solution after fermentation gave a reading in a 200 mm. tube of -0.1 division, and 40 c.c. were required to reduce 10 c.c. of Fehling's solution. Opposite 40 c.c. in col. I of the Table is the factor 0.1319, the reducing power of the unfermentable residue in 10 per cent. solution expressed as percentage of apparent invert sugar. In 0.2 per cent. solution, therefore, the unfermentable matter would raise the apparent content of invert sugar 0.0026 per cent. In a concentration such that 10 c.c. of Fehling's solution require from 36 to 37 c.c., a difference of 0.0037 per cent. of invert sugar makes a difference of 1 c.c. in the burette reading (see Table, col. I); unfermentable reducing substances equivalent to 0.0026 per cent. invert would therefore reduce it 0.70 c.c. 10 c.c. of Fehling's solution would therefore require $(36.45 + 0.70 =) 37.15$ c.c. of the 0.2 per cent. solution if this were free from unfermentable reducing substances, or 1 g. of the sample contains dextrose and lævulose equivalent to $10 \div (37.15 \times 0.002) = 10 \pm 0.0743 = 134.6$ c.c. Fehling's solution.

In concentrations such as that in which the first reduction experiment was made—namely, where 10 c.c. of Fehling's solution require 36.45 c.c. of sugar solution—1 g. dextrose = 196.6 c.c. Fehling's solution and 1 g. lævulose = 183.8 c.c. Fehling's solution (cols. D' and L' of the Table); but 1 g. of the sample requires 134.6 c.c. of Fehling's solution. If the percentage of dextrose in the sample is represented by D and the percentage of lævulose by L, the equation is:—

$$1.966 D + 1.838 L = 134.6 \quad (1)$$

The sample was found to contain 0.9 per cent. of sucrose; a 0.9 per cent. solution of sucrose gives a reading of $(3.85 \times 0.09 =) +0.3$ division when read in a 200 mm. tube in the Ventzke polarimeter. The actual reading (-4.7) must therefore be corrected for this amount, as well as for the reading of the unfermentable residue (-0.1), in order to arrive at the reading due to the dextrose and lævulose alone:—

$$-4.7 - 0.3 - (-0.1) = -4.9 \text{ divisions.}$$

Since 1 per cent. solutions of dextrose or lævulose give readings of 3.05 and -5.32 divisions respectively, then:—

$$0.305 D - 0.532 L = 4.9 \quad (2)$$

From the above two equations, $D = 39.0$ and $L = 31.5$.

The Table made use of above was constructed from experiments

made by the authors with Fehling's solution, of which 10 c.c. required 25.65 c.c. of 0.2 per cent. pure invert sugar solution when using ferrous thiocyanate as the indicator and conducting the titration as prescribed in the section on "Sugar," this Vol., p. 564. If different Fehling's solution requires say only 25 c.c. of 0.2 per cent. invert sugar, to use the Table it will only be necessary to reduce the numbers in cols. D, L, I, and M, and increase those in cols. D', L', I', and M' proportionately.

5. Unfermentable Carbohydrates.

These are estimated indirectly by deducting from 100 the sum of the percentages of dextrose, lævulose, sucrose, albuminoids, ash, and water.

Invert sugar is supplied to the brewer in three grades, and the following are typical analyses of each:—

	No. 1	No. 2	No. 3
Dextrose	36.85	36.96	35.44
Lævulose	36.22	35.01	34.85
Sucrose	3.39	1.89	4.54
Albuminoids	0.20	0.26	0.27
Ash	1.57	2.20	2.51
Other organic matter *	4.25	5.23	3.60
Water	17.52	18.45	18.79
	100.00	100.00	100.00

	No. 1	No. 2	No. 3
* Containing unfermentable reducing carbohydrates expressed as invert sugar	3.36	3.62	3.40 p.c.
Brewers' extract per 2 cwt.	72.8	72.6	72.6 lbs.
Tint (Lovibond, 10 p.c. solution 1" cell)	3.5	8.5	13.0 N.
Specific rotatory power $[\alpha]_D$	-11.6°	-11.4°	-10.4°
Iron oxide (Fe_2O_3)	0.002	0.003	0.003 p.c.

I.—GLUCOSE AND OTHER STARCH SUGARS.

These sugars, prepared by the hydrolysis of different kinds of starch with acids, contain not only dextrose and water, but maltose and dextrans (or, more probably, malto-dextrans), ash constituents, and traces of albuminoid substances. Glucose chips, the most important brewing sugar after invert, contains 60 per cent. or more of dextrose, about 5 per cent. of maltose, and perhaps 15 per cent. of apparent dextrin. Glucose syrup or dextrin-maltose may contain as little as 23 per cent. of dextrose and as much as 27 per cent. of maltose, and generally over 32 per cent. of apparent dextrin.

The analysis of these products is conducted on the same lines as that of Invert Sugar (p. 823), but the inversion experiment for the estimation of sucrose is omitted, and, in the equations, the constants for maltose are substituted for those of lævulose. The equations are:—

$$\begin{aligned} \text{and} \quad & D + 1.225 M = G & (1) \\ & 0.305 D + 0.798 M = R & (2) \end{aligned}$$

where G is the gram Fehling equivalent of the sugar as experimentally determined (*cf.* Invert Sugar) and R the observed rotation of a 10 per cent. solution less the rotation due to unfermentable substances. The coefficient of D in equation (1) is derived from col. D of the Table as described under Invert Sugar. The coefficient of M is a constant independent of concentration.

The following is an analysis of a high grade sample of glucose chips:

Dextrose	66.76
Maltose	3.96
Albuminoids	0.53
Ash	1.75
Dextrinous carbohydrates and other organic matter	13.60
Water	13.40
	<u>100.00</u>
Brewers' extract per 2 cwt.	76.1 lbs.
Tint (Lovibond, 10 p.c. solution 1" cell)	10.0 N.
Specific rotatory power	$[\alpha]_D 50^\circ 8$

This analysis can scarcely be taken as typical, since these products vary enormously in composition. Thus, the content of total sugars ranges from 65 to 75 per cent., and the extract from 72 to 76 lbs. The percentage of maltose may also vary from 12 per cent. to nil. The specific rotatory power ranges from $[\alpha]_D 44^\circ$ to 56° .

A typical analysis of glucose syrup, the composition of which is remarkably constant, is the following:—

Dextrose	23.10
Maltose	26.03
Dextrin	32.17
Albuminoids	0.22
Ash	0.48
Water	18.00
	<u>100.00</u>
Brewers' extract per 2 cwt.	70.7 lbs.
Specific rotatory power	$[\alpha]_D 113^\circ 1$

K.—HOPS.

The following methods of examination are those most commonly employed, or in the writers' opinion the most valuable.

1. Estimation of Hard and Soft Resins.

In Great Britain this is usually carried out by the method of L. Briant and C. S. Meacham.¹ A weighed quantity (3 or 4 g.) is placed in a paper thimble in a 100 c.c. Soxhlet apparatus and extracted with petroleum spirit (b. p. about 50°) for twenty-four hours. The petroleum

¹ *J. Fed. Inst. Brewing*, 1897, 3, 233.

spirit extract is filtered, if necessary, from particles of hop, the bulk of the solvent distilled off, and the residue of *soft resins* dried to constant weight in an oven maintained at about 60°.

After removal of the soft resins with petroleum spirit the hops are extracted for twelve hours with ordinary ether. The ethereal extract is treated precisely like the petroleum spirit extract and the dried extract is weighed and returned as *hard resin*.

Alternative methods and a method for the separate estimation of the two (α and β) soft resins have been proposed,¹ and methods depending on extraction with petroleum spirit have also been criticised recently by F. B. Power, F. Tutin, and H. Rogerson,² who isolated notable quantities of fatty acids from the petroleum spirit extract of hops. Since a condition precedent to this isolation was hydrolysis with alcoholic potash, it by no means follows that the resinous material contains a large proportion of fatty acids as such. It has long been known that one of the soft resins (the so-called α -resin) and the well characterised α -acid closely related to it yield valeric acid and a hydroxyketonic acid of high molecular weight when hydrolysed with potassium hydroxide,³ and more recently it has been shown that the "soft resin" may be contaminated by a fatty oil derived from crushed seeds.⁴ Crushed seeds, however, are rarely present in considerable number, and the fact remains that the above test, which is in most general use in this country, has done, and continues to do, very good service from the technical point of view, the preservative properties of hops being more or less proportional to the content of soft resins. The hard resins are probably oxidation products of the soft resins and are believed to be useless to the brewer. Their estimation, however, assists in deciding whether a deficiency of soft resins is the fault of the original hop, or due to prolonged storage, or to storage under bad conditions.

2. Direct Estimation of Antiseptic Power of Hops.

A biological method, first described by A. J. Brown and G. B. Ward,⁵ promises with further experience to prove of great value, either as amplifying, or possibly replacing, the estimation of soft resins. Since it has not yet been standardised, as it must be before it can pass into general use, the method will not be described here, but its potentialities are so great that reference to the above paper and to a later one by A. J. Brown and D. Clubb,⁶ are fully justified. In the discussion of the latter paper suggestions for standardising the method were made (*loc. cit.*), somewhat on the lines of the Rideal-Walker method for disinfectants.

¹ Cf. Article on "Hops" by G. C. Jones, Allen's *Commercial Organic Analysis*, vol. vii., 1913.

² *J. Chem. Soc.*, 1913, **103**, 1267.

³ Lintner and Schnell, *Z. ges. Brauw.*, 1904, **27**, 666.

⁴ Briant and Harman, *J. Inst. Brewing*, 1910, **16**, 5.

⁵ *J. Inst. Brewing*, 1910, **16**, 641.

⁶ *Ibid.*, 1913, **19**, 261.

3. Estimation of Moisture.

This is carried out in many laboratories by drying 3 g. *in vacuo* over sulphuric acid. The method is a good one, but almost identical results may be obtained by drying for three hours in a vigorously boiling and well-ventilated water-oven.

4. Detection of "Sulphuring."

Some confusion exists on this subject in the text-books, which use this term indifferently to designate two entirely different practices. In England a certain quantity of sulphur is usually thrown on the fire of the drying kilns towards the end of the drying process. The resulting sulphur dioxide tends to restrict the subsequent development of moulds and other objectionable micro-organisms, and, in so far as it does this, its action is, of course, useful. The grower's chief motive for the use of sulphur on the kiln, however, is the improvement it effects in the appearance of his hops. If this misleads the brewer in his choice of hops, the practice is not free from objection, but possibly the antiseptic value of sulphur dioxide outweighs the objection attaching to the production of a fictitious appearance. Brewers here and there attribute occasional yeast difficulties to the use of heavily sulphured hops, but the evidence of causal connection is seldom very strong when investigated. Continental works devote considerable space to the detection of this kind of sulphuring, but the practice being nearly universal here, nothing less than a quantitative estimation could have much value. This, however, is seldom called for.

Detection of Free Sulphur.—The other practice referred to as "sulphuring" is that of dressing the growing hops with flowers of sulphur to arrest the development of mould. It has been said that when hops have been heavily sulphured in the field, their use in the brewery has given rise to "stench," owing to the sulphur finding its way to the fermenting vessels, and, in contact with living yeast, being reduced to hydrogen sulphide. It is possible for sulphur as such to find its way on to the hops during the kilning process also, if the sulphur used in that process be unskillfully applied.

For the detection of sulphur in hops, the method most commonly in use is to heat 5 g. with 250 c.c. of water and 5 g. of slaked lime in a beaker which is placed in a boiling water-bath for twenty minutes. A portion of the solution is filtered, cooled, and tested at once with a freshly prepared, dilute solution of sodium nitroprusside. Nearly all English hops when tested in this manner give a red coloration. An experienced worker may decide from the intensity of the colour whether the hops can properly be described as containing notable or excessive amounts of free sulphur. The coloration is transient and

could not easily be made the basis of a quantitative method with any pretensions to accuracy.

Estimation of Free Sulphur.—For this estimation the hops are extracted with xylene in a Soxhlet or other extractor, a piece of bright copper foil (reduced in hydrogen) having been first placed in the flask and weighed with it before adding the xylene. The xylene dissolves the sulphur, which at the temperature of boiling xylene combines with the copper to form copper sulphide, which in small quantity is fairly adherent. A dozen syphonings are more than sufficient. The foil is washed a few times by decantation with small quantities of xylene, then with petroleum spirit, and the flask dried in a steam-oven, allowed to cool, and weighed.

5. Physical Examination of Hops.

This examination is more important than the physical examination of malt or barley, because, whereas malt and, to a less extent, barley can be valued by chemical tests alone, a sample of hops with a very high percentage of soft resins may be in some respects of less commercial value than another sample containing less soft resin, for the deciding characteristic in such a case may be that of aroma or flavour.

Concerning the aroma of hops, nothing useful can be written, but the following notes may be of some value.

The brewer gives preference to a whole hop and a sticky hop. Good, fresh samples of individual hops, rich in lupulin, stick together, and only slowly open out again when pressed tightly in the hand, although, as a whole, a properly dried sample is very elastic and springy.

An examination of the lupulin glands (the pollen-like grains conspicuous in a good hop) with a lens is useful. In fresh, well-managed hops, these are of a golden yellow colour, with slightly wrinkled surfaces and oily contents that readily ooze out under pressure. With age they become more wrinkled and darker in colour, assuming finally a deep red-orange tint. Too high drying induces changes in appearance similar to those that naturally result with age.

A good sample should be bright in colour, a dull, rusty appearance being generally an indication of a damaged hop, but a brown-coloured hop is not necessarily objectionable, nor will it give increased colour in the copper if the brownness be merely due to ripeness. An exceptionally pale colour may not improbably correspond to picking while still unripe before the full development of the preservative resins. The colour of the foliage leaves which may be found in the sample affords a guide as to the manner in which drying has been conducted. These leaves should be of a fresh, lively green colour, not dirty brownish or olive-green.

Interpretation of Results of the Chemical Analysis of Hops.—

Good, new hops, according to their origin and the season, may contain from 11 to 16 per cent., or even more, of soft resins, and 3 to 6 per cent. (usually 3 to 4 per cent.) of hard resin, as determined by the method of Briant and Meacham. In three years under average storage conditions where no cold store is available, the sum of the soft resins may fall as low as 4 per cent., and the percentage of hard resin may rise to more than 10; but the increase of hard resin never quite equals the decrease of the others, so that the sum of the resins tends to decrease and in some cases decreases rapidly. In Great Britain to-day, however, hops are usually cold-stored, and the deterioration is then very slow. Hops have been kept in cold store for five or six years without the loss of even 0.5 per cent. of soft resin. Regarded as an antiseptic, such hops still possess a high value, but it must not be supposed that their commercial value is equal to that of good new hops, for during so long a period of cold storage the aroma is lost to a considerable extent.

The drying process, as usually conducted in England, reduces the moisture in hops from 60 or 70 per cent. to less than 6 per cent. By subsequent exposure on the packing floor, the moisture always rises somewhat, and, if the time of exposure be long and the atmosphere very moist, it may rise to 12 per cent. or more. Such hops do not keep well, and hops containing more than 11 per cent. of moisture should not be bought except for immediate use, and, of course, only if suitable in other respects. On the other hand, hops containing much less than 8 per cent. of moisture are inclined to be brittle and scarcely bear handling without risk of falling to powder. Not only does such breaking up imply risk of loss of lupulin, but the brewer has a preference for whole hops for other good and sufficient reasons.

II. BEER.

1. Original Gravity.

The meaning of this expression—the specific gravity of the wort from which the beer was made—is explained in the introduction to this section. As the duty on beer is based on the strength of the wort as measured by its specific gravity before fermentation, it becomes necessary to estimate the original gravity of beers intended for export, so as to calculate the drawback. The figure is also of value for other purposes.

When beer wort is fermented, the principal change is the production of alcohol and carbon dioxide from maltose. The loss of the latter decreases the specific gravity, and the presence of alcohol still further depresses it. If these were the only changes, the determination of original gravity would present no difficulty. It would only be

necessary to distil 100 c.c. until all the alcohol was over, make up the distillate and the residue each to 100 c.c., and determine their specific gravities. From that of the distillate, the alcohol present could be derived from Tables, the equivalent amount of maltose calculated, the excess gravity of a solution of this quantity of maltose in 100 c.c. calculated from the known solution factor of maltose, and the result added to the specific gravity of the residue in the still after dilution to its original volume.

In practice such a method would lead to erroneous results, because fermentation is less simple than was assumed in the foregoing paragraph. As the result of direct experiment, Graham, Hoffmann, and Redwood worked out the following method, which is the only one legalised for purposes of excise, though it is now known that it gives results about 2° too low. Recent research by Sir Edward Thorpe and H. T. Brown has furnished information for correcting the Tables, but pending legislation embodying such corrections, the Tables given below must be used in all work connected with the departments of Customs and Excise. In other cases, 2° may be added to the result obtained, and a note to this effect appended to the certificate of analysis.

The carbon dioxide is first removed from the beer by pouring it from one beaker to another, or by filtering through paper or a plug of glass wool.

100 c.c. is then introduced into a "Revenue still," diluted with 40 c.c. of water and distilled until about 80 c.c. has been collected. The distillate and the cooled residue are then each made up to 100 c.c., and the specific gravity of each is determined. When the specific gravity of the distillate (water=1000) is subtracted from 1000, the difference gives the degrees of "spirit indication." By reference to Table 62 (p. 834), the number of degrees of gravity lost during fermentation which correspond to this spirit indication may be found. This number plus the specific gravity of the residue in the still (after dilution to 100 c.c.) gives the original gravity of the beer.

The experimental data on which this Table was constructed included the formation of acid equivalent to 0.1 per cent. acetic acid, and no correction is necessary in the case of beers containing about this proportion. Any excess of acidity over 0.1 per cent. is supposed to be formed at the expense of the alcohol in the beer, and must be estimated and allowed for. The acidity of beer is estimated by titration with $N/10$ ammonia, using litmus paper as outside indicator, and is calculated as percentage of acetic acid. From the result 0.1 is subtracted, and reference is then made to Table 63 (p. 834), which shows for each 0.01 per cent. excess of acid up to 1.09 per cent. the addition which must be made to the degrees of spirit indication as determined from the specific gravity of the distillate.

Table 62.

Spirit Indication Table showing Degrees of Gravity Lost in Malt Wort during Fermentation.

Degrees of spirit indication.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	...	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·7	75·3	75·9

Table 63.

Acid Correction Table showing Additions to be made to Spirit Indication for Small Increments of Acidity in excess of 0.1 per cent.

Excess per cent. of acetic acid in beer.	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
·0	...	0·02	0·04	0·06	0·07	0·08	0·09	0·11	0·12	0·13
·1	0·14	0·15	0·17	0·18	0·19	0·21	0·22	0·23	0·24	0·26
·2	0·27	0·28	0·29	0·31	0·32	0·33	0·34	0·35	0·37	0·38
·3	0·39	0·40	0·42	0·43	0·44	0·46	0·47	0·48	0·49	0·51
·4	0·52	0·53	0·55	0·56	0·57	0·59	0·60	0·61	0·62	0·64
·5	0·65	0·66	0·67	0·69	0·70	0·71	0·72	0·73	0·75	0·76
·6	0·77	0·78	0·80	0·81	0·82	0·84	0·85	0·86	0·87	0·89
·7	0·90	0·91	0·93	0·94	0·95	0·97	0·98	0·99	1·00	1·02
·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

An example will perhaps make more plain the use of the Tables and the calculation of the results.

Specific gravity of water at 60° F.	1000·00
Specific gravity of distillate at 60°/60° F.	988·88
Difference=spirit indication	11·12
Correction for 0·24 per cent. <i>excess</i> of acid (from Table 63)	·32
Corrected spirit indication	11·44
Equal by Table 62 to degrees of gravity lost	51·4
To which add specific gravity of extract at 60°/60° F.	1041·6
Original gravity of wort.	1093·0

2. Alcohol.

This is estimated from the specific gravity of the distillate (obtained as in the determination of original gravity) by reference to alcohol Tables connecting specific gravity with percentage of alcohol by weight (see section on "Alcohol, Potable Spirits, and Liqueurs," this Vol., p. 711).

3. Extract.

For this estimation some of the beer is boiled to expel alcohol, made up to its original volume, and the specific gravity taken. If the original gravity has been determined, no special experiment is needed. The excess gravity over water (=1000) divided by 4 gives the percentage of extractive matters in the beer with sufficient exactness. The organic solids have a solution factor which closely approximates but is less than 4, whereas the mineral matters, present in smaller amount, have a much higher solution factor.

Methods for the estimation of "apparent maltose" and "apparent dextrin," and for the estimation of carbon dioxide, may be found in the special text-books (see Literature), in which detailed methods for the analysis of beer and malt worts are described. Such analyses are, however, somewhat beyond the scope of this section. The following test of the stability of beers must, on the other hand, be briefly mentioned.

4. Forcing Test.

Samples of the beer are placed in carefully cleaned conical flasks fitted with rubber stoppers carrying tubes which just penetrate the cork internally, and externally are bent twice at right angles, the vertical limb dipping into a cup or trough of mercury. The flasks are kept at a temperature of 80°-85° F. (26°·7-29°·4 C.) in an incubator, or by standing on a large metal hot-water plate, known as a "Forcing Tray." The period of incubation varies with the type of beer, export beers being submitted to much more prolonged treatment than beers intended for rapid consumption. The specific gravity of the beer ("apparent gravity"), acidity, flavour, odour, and condition are recorded before and after the test, and the sediment which is formed is carefully examined for wild yeasts and bacteria. Beers for export purposes and stock ales and stouts should be perfectly sound, and the sediment free from bacteria after four weeks; India pale ales should stand three weeks; light bottling beers a fortnight, and running mild ales and porter a week. Full use of the test can only be made by those experienced in it, but it can always be carried out by those with less experience, and the numerical data—loss of gravity and increase of acidity—obtained.

Typical Analyses of Beer.

	Original gravity of Wort.	Alcohol.	Total solids.
		Per cent.	Per cent.
Mild ale	1.055	4.5	5.9
Pale ale	1.061	5.4	5.3
Strong ale	1.100	8.9	8.5
Light dinner ale	1.040	3.5	3.5
Porter	1.055	4.0	6.6
Extra stout	1.074	5.9	7.6
Pilsener	1.042	3.4	4.5
Munich lager	1.052	3.4	6.9
Munich export	1.060	4.2	7.5

Estimation of Arsenic in Brewing Materials and Beer.

Since the unfortunate epidemic of arsenical poisoning in 1900, this has formed part of the routine of every brewing laboratory.

The method of analysis usually adopted need not be described in detail here, as it does not differ in essentials from the method employed in estimating minute traces of arsenic in other materials, as described in the section on "Sulphuric Acid Manufacture," Vol. I., pp. 362 *et seq.* The Marsh-Berzelius method is almost invariably employed, and the deposits obtained in tubes of small bore (2 mm.) are compared with standards obtained from known quantities (0.002 to 0.02 mg.) of arsenious oxide.

Whole Malt (25 g.) is treated with 50 c.c. of hydrochloric acid of sp. gr. about 1.05, previously heated to 50°. After twenty minutes the unabsorbed liquid, which measures rather more than 40 c.c., is poured off and 20 c.c. (= 10 g. malt) introduced into the Marsh apparatus. If a heavy mirror results, the test is repeated with 10 c.c. or 5 c.c. of the solution. All British malt contains a detectable trace of arsenious oxide, derived from the fuel used in drying it, but amounts in excess of $\frac{1}{200}$ grain per pound¹ are rare. Nevertheless, the test should never be omitted.

Hops may be tested in a similar manner, that is to say, the acid extract may be introduced directly into the Marsh apparatus, but a smaller quantity of hops must be taken, as 50 c.c. of liquid will not cover 25 g. of hops. The destruction of organic matter in hops, prior to the introduction of the extract into the Marsh apparatus, is considered necessary by many chemists, but the experience of the authors, confirmed by that of A. C. Chapman,² is that no more arsenic is found

¹ The Royal Commission on Arsenical Poisoning recommended a limit of $\frac{1}{100}$ grain per pound for solid foods and materials for the manufacture of foods and beverages, and $\frac{1}{100}$ grain per gallon for liquids intended for human consumption.

² *Analyst*, 1913, 38, 599.

in this way. Hops very frequently contain more than $\frac{1}{100}$ grain of arsenious oxide per pound. They are used, however, only to the extent of 1-5 lbs. per barrel by the brewer.

Brewing Sugars (including caramel which is made from glucose) may be introduced in 20 per cent. solution direct into the Marsh apparatus. Sugars of British manufacture to-day contain, as a rule, extremely minute amounts of arsenic (derived from the mineral acid used for inversion or saccharification), but British caramel may be made from foreign glucose, and foreign glucose is supplied as such to brewers. In no case should the test be omitted.

Beer is often introduced directly into the Marsh apparatus, but some beers at any rate, especially those of high gravity, do not appear to yield the whole of their arsenic when tested in this way. It is extremely rare now for beer to contain anything approaching $\frac{1}{100}$ grain of arsenious oxide per gallon, and the rigid control maintained over all brewing materials, including salts used for hardening water, yeast foods, sulphites used for sterilising plant or as preservative, is usually so strict that the freedom of the beer from dangerous amounts of arsenic can be safely assumed, at least by the producer, or he is content to test his beers without destruction of organic matter. No large amount of arsenic could escape him, and if any is found, further experiment, after destruction of organic matter, would be made. The outside analyst, if called on to estimate arsenic in beer, had best follow the directions given in the *Report of the Royal Commission on Arsenical Poisoning*, 1903, *Appendix 21*, p. 213, where alternative methods for the destruction of organic matter are described.

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PAPER

By Prof. W. HERZBERG, Director of the Department for the Technical Examination of Paper and Textiles, the Imperial Testing Station, Gross-Lichterfelde. English translation revised by C. F. CROSS, B.Sc., E. J. BEVAN, and W. BACON, B.Sc.

THE DETERMINATION OF MINERAL CONTENTS.

FOR an exact determination 1-2 g. of paper are dried at 100° - 105° , and after weighing, are burnt off until the ash is constant.

If the colour of the paper indicates a possibility of lead chromate being present as a pigment, the ash must be determined in a porcelain crucible.

The amount of ash found seldom corresponds to the amount of loading present as such in the paper, owing to the changes undergone in incineration. For example, china clay, which has approximately the chemical composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, loses its water of combination, and barium sulphate (blanc fixe) is partly reduced to sulphide by the carbonaceous matter. If the former type of loading be used, an allowance of 12-15 per cent. can be made, and a fairly true value of the loading in the original paper is then obtained. By the addition of 2 or 3 drops of concentrated sulphuric acid to an ash containing blanc fixe, the barium is reconverted into the sulphate and the excess of sulphuric acid may then be driven off over a Bunsen burner.

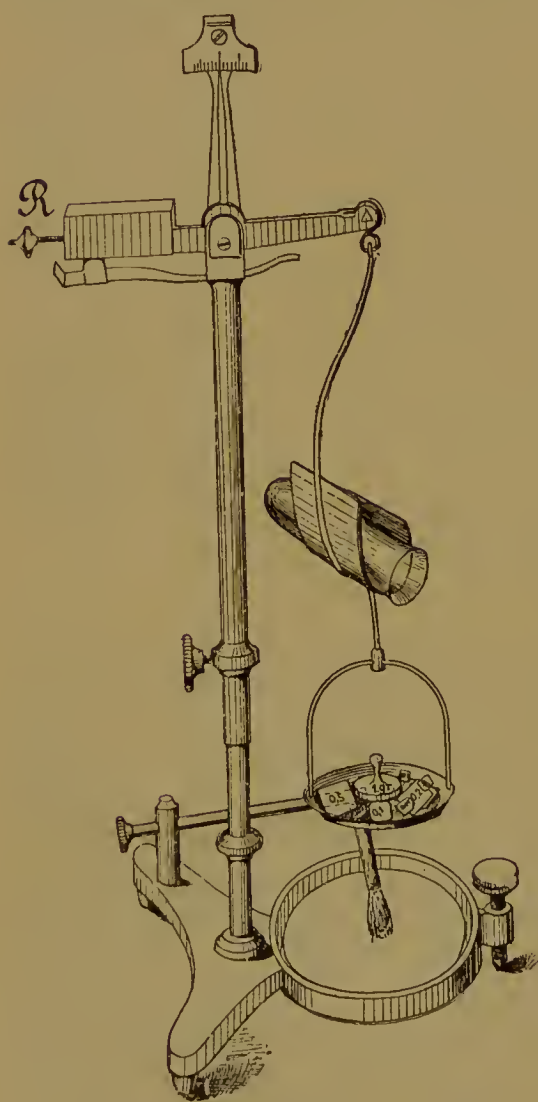


FIG. 79.

In practice, where a very exact determination of the ash is not required, Reimann's balance (Fig. 79), which gives results within 0.25 per cent. of the true value, may be employed.

In this balance an adjustable weight is attached to one arm of the beam, and the other carries two scale pans, one suspended directly above the other. The upper pan is used for holding a glass tube, and the lower pan for the weights required in the operation. As the balance without the glass tube requires a load of about 21 g. to bring the whole system into equilibrium, a tube is used of about 19 g. weight without, however, exceeding this limit. Upon the lower scale pan are placed 2 g. in weight made up of a 1 g. weight and the rest in decigram and centigram pieces; any deficiency may be made up with tiny pieces of lead. The whole system may then be brought into equilibrium by means of a regulating screw R carried on the other arm.

The attachment of a brush, as shown in the figure, is useful for putting on or taking off weights.

For the ash determination, 1 g. of paper is rolled up and put into the platinum wire net (Fig. 80) and burned. The ash is then shaken into the glass tube (Fig. 81) and its weight in centigrams determined. This gives directly the percentage of ash.

FIG. 80.



FIG. 81.



FIG. 82.

The determination of ash proceeds all the more quickly and thoroughly, the more easily the air can pass through. In order to obtain the results expeditiously, L. Schopper has constructed an apparatus by means of which air passes through the ash, and thence through a chimney-like superstructure. This apparatus (Fig. 82) has proved to be very satisfactory, and essentially reduces the time of heating. For the determination, 1 g. of paper is rolled up and put into a tube of thin iron sheeting, the latter fitting loosely into a short, horizontal tube of the "chimney"; the former can be removed and is closed by a wire net at the back. This tube is heated strongly by a burner, the products of combustion passing through the chimney, and, owing to the good supply of air, the burning is completed in a very short time.

Recently Schopper has devised a special apparatus for the burning of millboards, to which a balance provided with a pointer is attached; from the position of the latter, the percentage of ash can readily be observed. Schopper has also brought out electrical heating appliances for this work.

THE MICROSCOPICAL EXAMINATION OF THE FIBROUS CONSTITUENTS OF PAPER.

The microscopical examination serves to establish the particular fibres constituting the "furnish" of a paper, also the ratio of the same, and the condition of beating obtained in the manufacture. Only the most important types of fibres, such as linen, hemp, cotton, wood, straw, esparto, jute, and mechanical wood are dealt with in this section.

Preparation of the Paper for Examination.

According to the thickness of the paper, 2-5 sq. cm. are boiled up in a beaker for a minute or so with a 2-4 per cent. solution of potassium or sodium hydroxide, and, whilst hot, shaken vigorously. The alkali is then removed by washing the fibre thoroughly upon a fine wire mesh sieve.

Parchment paper cannot be readily pulped by the foregoing treatment, and the resolution of such paper is best effected by the method suggested by C. Bartsch, namely, by heating the paper to 50°-60° for two to five minutes, according to the degree of parchmentsing, in a mixture of equal parts of sulphuric acid and water. If the paper, when rubbed with a glass rod, appears to be sufficiently resolved, the fibre is filtered off and washed. If the resolving action has been too severe, it will be seen that the fibres are very short when examined under the microscope, and the time of heating and concentration must then be modified accordingly.

Materials containing wool should not be heated with alkali but only with water.

Chlor-zinc iodine or iodine dissolved in potassium iodide are most generally used as mounting solutions for the identification of the fibres.

The iodine solution consists of 6 parts of iodine, 10 parts of potassium iodide, 10 parts of glycerol, and 90 parts of water.

The chlor-zinc iodine is made by mixing 100 parts of zinc chloride, 10.5 parts of potassium iodide, 0.5 parts of iodine, and 75 parts of water; the mixture is set aside for some time, the clear solution poured off from the deposit, and a small crystal of iodine added.

The colour reactions with the various fibres when treated with these reagents are given in the following Table.

Fibres.		Colour in iodo-potassium iodide solution.	Colour in chlor-zinc iodide solution.
Group 1 (Rag class)	Linen and hemp . . .	Pale to dark brown . .	Weak to strong wine-red
	Cotton	Thin - walled fibres almost colourless	
Group 2 (Cellulose)	Wood and straw . . .	Grey to brown	Blue to red-violet
	Jute cellulose	Grey	Blue to blue-violet
	Esparto cellulose . .	Partly grey and partly brown	Partly blue and partly wine-red
Group 3 (Lignified fibres)	Mechanical wood, raw jute, and incompletely resolved wood cellulose	Partly a bright yellow-brown, partly yellow, according to thickness of layer and degree of lignification	Lemon to dark yellow
	Straw	Partly yellow-brown, partly yellow, partly grey	Partly yellow, partly blue, partly blue-violet

If the normal bast fibres are blue, the solution is too concentrated, and must therefore be diluted very cautiously with water until the fibres stain up the usual red colour.

If, on the contrary, the wood cellulose fibres are not blue but of a reddish colour, the solution is too weak and can usually be brought up to the required strength by the addition of a small quantity of zinc chloride. In some cases, however, the solution is not satisfactory, and it is better to make up a fresh one.

H. Jenke¹ recommends observing fibres in the following solution :— 50 c.c. of a saturated solution of magnesium chloride and 2.5 c.c. of iodo-potassium iodide solution (2 g. potassium iodide and 1.15 g. iodine in 20 c.c. of water).

The resulting colorations are then as follows :—

Rag fibres.	Brown.
Straw cellulose.	Blue-violet.
Wood cellulose.	Colourless to weak red.
Mechanical wood and raw jute.	Yellow.

H. Behrens² has proposed to employ the different absorbing properties of fibres for certain colouring matters as a means of identification. In this way variations of colour are said to be obtained which may certainly be useful in some cases.

E. Selleger³ immerses the fibres in a solution of calcium nitrate made

¹ *Papier-Zeit.*, 1900, p. 2867.

² *Microchemische Analyse.*

³ *Papierfabrikant*, 1903, p. 425.

up of 100 g. of dry calcium nitrate, 90 g. of water, and 3 c.c. of iodine solution (1 g. iodine, 5 g. potassium iodide in 50 c.c. of water).

The colorations obtained are :—

Rag fibres.	Wine-red.
Pine cellulose, unbleached.	Clear lemon-yellow.
Pine cellulose, bleached.	Pink with a violet shade.
Straw cellulose.	Blue.
Foliage celluloses.	Blue.
Mechanical wood.	Yellow.

In the estimation of the different kinds of fibres it is necessary not only to give careful attention to the colour and the structure of each fibre, but also to the ratio of each.

The following are the most important characteristic anatomical features.

Mechanical Wood, which is obtained by a mechanical grinding of pieces of wood, usually pine wood, consists of irregular fragments of fibres or fibre bundles, in which are seen characteristic pores (Fig. 83) and numerous medullary rays. When teased out a whole ultimate fibre is seldom obtained.



FIG. 83.

Wood Cellulose is usually produced like mechanical wood from fir or pines, and is differentiated from the former by the great breadth of the single cells. The canal is usually wide and the ends of the fibres are rounded or slightly tapered. The bordered pits of the pine cellulose (Fig. 84) and the vessels of the foliage woods are characteristic.



FIG. 84.



FIG. 85.

Jute (various species of *Corchorus*) consists of bast fibres either isolated or aggregated together as filaments. It is differentiated from other fibres in that the canal alternately constricts and expands in equally thickened parts of the ultimate fibre; in some cases the constriction is so pronounced that the canal is seen as a dark line (Fig. 85).

Straw Cellulose.—The bast cells (Fig. 86, *b*), which constitute the main portion of straw cellulose, are usually rather narrow and cylindrical, and show needle-like pointed ends. The occurrence of the wavy-edged,

cuticular cells and also of the thin-walled, short, parenchymatous cells with rounded ends are characteristic (Fig. 86, *a* and *c*).

Esparto Cellulose is obtained from the grass (*Stipa tenacissima*) which occurs in large quantities in Africa and Spain. The cuticular and bast cells are similar to those of straw, but of smaller dimensions

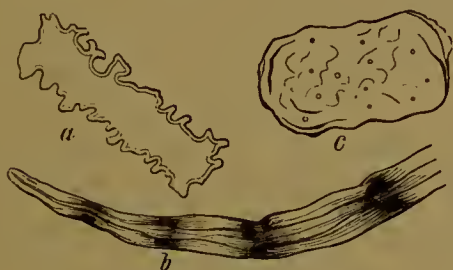


FIG. 86.



FIG. 87.

(Fig. 87, *a* and *b*). Esparto is differentiated from straw by small tooth-shaped cells (leaf hairs, Fig. 87, *c*) as well as by the absence of the large parenchymatous cells. A further noticeable difference is the irregular coloration in a portion of the bast fibre.

Linen.—The bast cells of flax are narrow and cylindrical, with sharp-pointed ends and node-like swellings distributed along the fibre (Fig. 88). The lumen is very narrow and usually appears only as a dark line. Since the ultimate fibre is long (from 4-70 mm.), it must essentially be cut and beaten up for use in paper; the fractured ends so formed are frequently characteristic of flax, and the fibre shows longitudinal striæ.



FIG. 88.

Hemp.—The hemp fibre is very similar to linen, and its identification in presence of the latter fibre is by no means easy.



FIG. 89.

Cotton.—The seed hairs of cotton are easy to recognise by the closely folded, utriculated shape of the cells. The canal is usually very broad, and the cell walls show reticulated markings (Fig. 89). The fibre is usually spiral-shaped, especially in the case of raw cotton (where it is very apparent). The natural ends of the ultimate fibre are rounded and are seen occasionally in cotton papers, but usually the ends show a more or less torn appearance.

The estimation of the proportions of various fibres present in a

paper is best carried out by a direct comparison with freshly prepared mixtures containing definite proportions of the various fibres.

The examination is carried out by mounting the fibres in a solution of chlor-zinc iodide, and observing the ratio of the various colour groups of fibres to each other under a magnification of 50-70. A comparison is then made against a standard mixture, made up as above, under a magnification of 150-200.

For a general examination as to the condition of beating, a magnification of 25 is used.

The expressions used in practice for the condition of the fibres, when used for certain papers, are "long," "short," "free," "greasy," or "wet," and if it be practically impossible to give a definite description of the condition of beating, it is best to compare such a paper with two or more definite pulp mixtures.

In commerce, for example, the question as to whether a paper is a pure rag paper or not, is frequently raised. In such a case the examination is confined simply to a microscopical test.

In such an examination, where it is not necessary to establish the source of individual fibres, but only to determine whether the fibres are of the rag class, a simple microscopical preparation serves. The teased-out fibres are worked up with chlor-zinc iodide solution, and examined under a low magnification. If the paper is of pure rag, all the fibres are coloured wine-red, since wood cellulose, whatever its source, turns blue with this reagent, and mechanical wood and raw jute turn yellow.

Since, in practice, the differentiation of any two or three groups of different fibres, *e.g.*, Rag, Chemical Wood, Mechanical Wood, that may be present in a paper depends upon the examination of the colour reactions obtained,—red, blue, or yellow,—it is easy to get a fair approximation to the relative quantities of each.

THE DEGREE OF LIGNIFICATION OF WOOD CELLULOSE.

In the manufacture of paper, various wood celluloses find application: some are fully purified cellulose, whilst others contain traces of the non-cellulose constituents. The latter depend upon the degree of resolution and bleaching which the wood substance has undergone. Bleached stuffs are usually free from the lignone complex, whilst unbleached or half-bleached stuffs show a more or less strong lignine reaction.

The coloration of the fibres with a solution of iodine frequently permits of a ready means of determining the extent of lignification. The identification is rendered still more easy by the use of certain colours.

P. Klemm's Method of Examination.

Klemm classifies the degree of purity to which the wood cells in wood cellulose have been brought according to the kind and depth of coloration produced with a saturated solution of malachite green in 2 per cent. acetic acid. The reagent is used both for microscopical preparations and macroscopic tests. The purer the cellulose the less the absorption of dye. In the higher grades of bleached wood cellulose the coloration is almost nil, with half-bleached cellulose it is sky-blue, and with unbleached cellulose deep green.

In order to see whether soda or sulphite wood cellulose is present, a second dyestuff is used in combination with malachite green. This second colour is a saturated solution of rosaniline sulphate made by dissolving the dyestuff in water containing 2 per cent. of alcohol, and adding sulphuric acid until the solution turns to a bright violet colour.

The cellulose is coloured as follows :—

- (1) Unbleached sulphite cellulose is coloured a deep red-violet.
- (2) Bleached sulphite cellulose takes up a more or less dark red to violet coloration.
- (3) Unbleached soda pulp is coloured somewhat less than bleached sulphite cellulose.
- (4) Bleached soda cellulose gives only a weak reddish colour, or usually no colour at all.

The application of rosaniline solution alone to the pulp cannot distinguish between bleached sulphite and unbleached soda pulp, but, according to Klemm, this can be effected when the test is followed by malachite green. If the cellulose is coloured red with rosaniline sulphate, and bright green with malachite green, it is unbleached soda wood pulp; if, on the other hand, the pulp is coloured red with rosaniline, but only a weak blue or not at all with malachite green, it is bleached sulphite cellulose.

The varying degrees of purity of the cellulose can perhaps be more easily distinguished by the fundamental method of Behrens for the differentiation of textile fibres by consecutive double staining with malachite green and Congo red. The material to be tested is resolved by boiling with dilute sodium hydroxide solution, then warmed for a few minutes with fifteen to twenty times its weight of a 0.5 per cent. solution of malachite green acidified with acetic acid, and after it has been well shaken up, washed with water on a sieve until the washings are practically colourless. An idea as to the extent of lignification of the fibres can be thus quickly obtained. If the fibres are highly lignified, they are coloured dark green; if only slightly lignified or quite free from lignin, they are stained a weak green.

For a further confirmation the dyed pulp is treated in a similar

manner with a 0.5 per cent. solution of Congo red to which has been added a few crystals of sodium carbonate. The dyed fibre is washed until the water is almost colourless. The doubly stained pulp is then mounted in water or in water and glycerine. The highly lignified fibres show up under the microscope as dark green, the less lignified fibres as blue to bright green, whilst the fibres free from lignin are red.

THE DIFFERENTIATION OF SULPHITE AND SODA WOOD CELLULOSE.

If wood celluloses are in the condition of pulp, it can be determined whether such a pulp is soda or sulphite cellulose. In doubtful cases the content of rosin can be estimated, as this is very different in the two cases. That of sulphite pulp usually approximates to 0.5 per cent., whilst in soda pulp it is about 0.05 per cent. The content of rosin in bleached sulphite is somewhat lower than in the unbleached, but the different methods of making pulp by any of the sulphite processes do not have any definite influence upon this factor.

C. G. Schwalbe¹ has used the so-called cholesterin reaction as a means of differentiating between sulphite and soda wood celluloses.

If rosin is treated with acetic anhydride and concentrated sulphuric acid, a rose-pink coloration is first formed, then a blue, and finally a green colour. Sulphite wood cellulose, on account of its higher content of rosin, shows this more clearly than soda wood cellulose; the former gives a distinct green, whilst the latter gives a yellow colour.

The test is carried out as follows:—About 0.5 g. of wood cellulose is extracted with 1-2 c.c. of boiling carbon tetrachloride or chloroform, the liquid poured into a dry dish, about 0.5 c.c. of acetic anhydride added, and finally, pure concentrated sulphuric acid is dropped in (about 6-10 drops). If a delicate rose-pink coloration ensues, which changes rapidly to a green, sulphite wood cellulose is present; soda wood pulp does not give this reaction, and at most only a turbid yellow colour is produced. The addition of sulphuric acid is so arranged that a separation into two layers is effected, the upper one of which is green, whilst the lower layer is colourless. The reaction is equally good for bleached or unbleached pulp.

THE MACROSCOPIC DETERMINATION OF MECHANICAL WOOD.

For the examination of a paper only for mechanical wood or other lignified fibres without a microscope, different reagents may be employed. A solution of phloroglucinol in alcohol, to which hydrochloric acid has been added, colours a mechanical wood paper a deep red, the depth of the colour depending on the amount present in the

¹ *Wochenblatt für Papier Fabrikation*, 1906, No. 34.

paper. An aqueous solution of aniline sulphate colours the paper a golden yellow. C. Wurster's "Di-papier" or "Di-solution" (dimethyl paraphenylene diamine), the former of which must be first moistened with water, when dropped upon a mechanical wood paper, produces orange-red spots which turn carmine-red on treatment with water. As the coloration is proportional to the amount of mechanical wood present, an approximately quantitative determination can be made by comparing the colour against a standard colour Table, or better still against papers containing known amounts of mechanical wood. It is to be borne in mind, however, that certain colours used in colouring papers (*e.g.* metanil yellow) give a red coloration with acids, and that consequently such a reaction may be occasioned by the hydrochloric acid used in the phloroglucinol solution.

DETERMINATION OF THE HARDNESS OF SIZE IN PAPER.

The estimation of the hardness of size in paper is best carried out by drawing lines 0.5, 0.75, 1.0, 1.25 mm. broad with a drawing pen, using some good commercial ink, and then allowing the ink to dry without blotting. With a "hard-sized" paper the edges of the lines should be sharp, and the ink of the lines 0.75 mm. broad or less should not have penetrated to the under surface even after twenty-four hours.

In former methods the hardness of the sizing was not determined by testing the ink, but with two colour reacting liquids, each drop of liquid being on opposite sides of the sheet; Leonhardi, Post, Schluttig-Neumann, and Kollmann have shown that such tests are not free from objections.

Klemm¹ has brought forward a new method, which is not merely confined to the capacity of the paper for resisting the penetration of ink, but also of other liquids, for example, oil, alkaline solutions, etc. He allows pieces of the paper under examination to float upon the liquid for varying times (two, five, ten, twenty minutes); the excess of liquid is then removed from the sheets by drawing the papers along the edge of the vessel, and finally the sections of paper are pressed between blotting paper. From a comparison of the test-piece in which the first penetration was noted, with the piece showing complete penetration, the resistance of the paper to the testing fluid may be judged.

THE EXAMINATION OF SIZE.

Animal Size (Gelatin).

The sizing with gelatin is carried out either by immersing the paper in sheets, or in a continuous web in a solution of size (surface or vat sizing), or by putting the size solution into the Hollander.

¹ *Wochenblatt für Papier Fabrikation*, 1908, p. 4118.

Papers which are heavily surface sized are clearly recognised by their hard "feel." If the sheet is pressed tightly together with moist fingers, it feels sticky and usually adheres to the fingers; if strongly breathed upon and rubbed, there is a smell of animal size. If a paper is written on after being rubbed and balled together, the ink runs and penetrates through the sheet.

The presence of gelatin is proved by various tests. One of the tests most commonly used on account of its simplicity, is to drop melted candle grease upon the paper. In the case of a rosin-sized paper, the fat penetrates the sheet, whilst in a gelatin-sized paper the grease remains on the surface. After removal of the solidified fat from the surface, the latter paper is quite opaque, whilst in the former, transparent grease spots show up clearly. In the application of this test it must be borne in mind that sometimes papers are made that are sized with rosin in the engine and subsequently with gelatin when the paper is made. Such papers behave as if sized with gelatin alone, *i.e.* the drops of melted fat do not penetrate. In such a case the examination for rosin is carried out by the method given on p. 849.

The confirmation of the presence of gelatin is usually made with tannic acid, which forms an insoluble compound with gelatin. If tannic acid is added to a not too dilute solution of gelatin, a thick, jelly-like precipitate is formed, and even after diluting largely with water, a milky turbidity is seen, which soon separates out as a flock. For the purpose of carrying out this test, the paper is extracted with distilled water, and the extract concentrated, whereby the reaction is obtained more easily; after cooling, solid ammonium chloride is added to the extract, and subsequently potassium iodide solution in slight excess. Dissolved starch, if present, is precipitated as the blue iodide of starch; this is filtered off, a few drops of a solution of alum added to the filtrate, and finally a solution of tannic acid. If the paper has been sized with gelatin, a more or less dense, flocculent precipitate is formed, either at once or after a few minutes.

A confirmation of this test can be made by filtering off the precipitate obtained as above, drying, and then heating it to redness with soda lime; ammonia is evolved if gelatin be present, which can be confirmed by turmeric or red litmus paper, in addition to the smell.

*Cross, Bevan, and Brigg's Method for the Quantitative Determination of Gelatin in Paper.*¹

The basis of the process is the following reaction. When chlorine is allowed to act upon gelatin, chloroamine (NH_2Cl) is formed by the

¹ *J. Soc. Chem. Ind.*, 1908, 27, 260.

interaction of the former with the albuminoids of the latter, which gives a blue colour with starch-potassium iodide.

If moistened pieces of paper are treated with chlorine, immersed in a 2 per cent. solution of sodium phosphate to remove the interfering iron compounds, and then into a solution of starch-potassium iodide, a blue coloration is formed at once in presence of traces of gelatin.

For the quantitative estimation, the moistened paper is treated with chlorine and then suspended in a steady current of air for at least one hour (by means of a fan or ventilator), to aid the removal of the chlorine. The paper is then torn up into small pieces and soaked in a $N/100$ solution of sodium arsenite for one hour. The excess of arsenite is titrated back with a standard iodine solution. According to the experiments of the authors, 100 parts of gelatin combine with 15.4 parts of chlorine.

Comparative experiments made by the above process and the Kjeldahl method show a fair agreement. As, however, the Kjeldahl process is free from objections and more easily carried out than the chloroamine method, the former is recommended.

Rosin Size.

Opinion, as to whether in the rosin sizing of paper the active factors are either free rosin, rosinate of alumina, or a mixture of both, is still divided. Wurster considers that the hardness of paper depends solely upon free rosin; others think that it is effected by a combination of the rosin with alumina.

There is no longer any doubt that in all cases free rosin is present as such in the paper, and upon this depends the methods for the detection of rosin size.

One of the oldest tests is based on the reaction that when an alcoholic solution of rosin is largely diluted with water, a milky turbidity ensues owing to the separation of rosin. Absolute alcohol is poured upon small pieces of paper torn from half of the sheets under examination, and the vessel (preferably a test tube) in which the extraction is carried on is heated for about fifteen minutes in hot water. If this extract is poured upon distilled water, the rosin separates out and forms a milky white turbidity. This reaction is not very sensitive, and is not clearly seen with only small pieces of paper. If, however, a few drops of hydrochloric or acetic acid be added to the alcohol before boiling, the combined rosin passes into solution and the turbidity is much more pronounced.

A very clear reaction is also obtained if the paper is extracted hot with pure glacial acetic acid, without the addition of alcohol, and the extract mixed with water; as little as 1 sq. cm. of the paper suffices for this test. Small pieces of the paper are boiled with 2-3 c.c. of acetic

acid, and distilled water added; if rosin is present, a dense white turbidity is formed. A faint opalescence of the liquid is not looked upon as a proof of the presence of rosin. Acetic acid itself dissolves, under these conditions, small quantities of other substances which give this opalescent appearance, *e.g.* the acid extracts entirely the small quantities of rosin in any mechanical wood that may be present and would also dissolve a small proportion of calcium sulphate loading, if such be used.

In such cases a faint opalescence occurs on dilution with water, but this can scarcely be confused with the reaction which is produced from rosin size. In order to remove any doubt, however, it is a good plan to evaporate to dryness a portion of the alcoholic or acetic acid extract, and thus to confirm the resinous character of the residue.

T. Morawski¹ proposed to apply the Storch reaction for the detection of rosin oil to the examination of paper for rosin size. Colophony (ordinary rosin) is dissolved in a dry tube by warming with acetic anhydride, and after cooling, a drop of concentrated sulphuric acid is poured cautiously into the tube; a red to blue coloration is formed which rapidly changes to a brown-yellow. The reaction, which is very sensitive, is carried out on 10 sq. cm. of paper.

Another method due to W. Herzberg,² which recommends itself on account of its great simplicity, is the following:—A piece of the paper under examination, about 7.5 cm. square, is laid upon a hollow support (*e.g.*, a glass dish, watch-glass, or beaker) and about 4-6 drops of ether are allowed to fall in the centre. The ether spreads more or less over the sheet and evaporates after a short time. The evaporation can be expedited by fanning or blowing air so that the whole operation takes scarcely fifteen to twenty seconds. In rosin-sized papers a more or less clearly marked margin of rosin is seen. If after the first evaporation no ring forms, it is a good plan to repeat the operation a second or third time. Papers sized with only a little rosin, *e.g.* in the case of papers containing both vegetable and animal size, the ring is not so clearly marked. Four different kinds of paper which were treated by the method described above, and then photographed by transmitted light, are shown in Fig. 90.

This method should prove exceedingly valuable in the examination of books, printed matter, manuscripts, maps, etc., as these can be subjected to such treatment without the removal of any part of the paper. The ring of rosin left upon the object under examination will not, in most cases, be objectionable. Where this might be the case, 1 drop of ether is sufficient, either for the original test or if the experiment is repeated.

¹ *Mitteilungen aus dem k. k. technologischen Gewerbe-Museum, Vienna*, 1888, Nos. 1 und 2, p. 13.

² *Mitt. k. Materialprüf.*, 1892, 10, 80; *J. Soc. Chem. Ind.*, 1892, 11, 638.

In certain special cases a choice of processes has to be made. If, for example, a grease paper is to be examined, the examination could not be carried out by extracting with alcohol or acetic acid, as the fat would also go into solution and subsequently give a turbidity with water. The ether drop method of Herzberg would also fail, as fat alone produces a ring. Thus only the Morawski reaction is left, and indeed here again it is necessary to presuppose that the fat present in the paper contains no rosin oil, for the latter gives the Morawski reaction.



FIG. 90.

With coloured papers also, not all of the prescribed methods can be applied. A choice must be made according to the behaviour of the dyestuff under the action of the reagents employed. In short, one general method for the detection of rosin in paper cannot be given, and due judgment must accordingly be exercised in the choice of the method to be applied.

For the estimation of rosin (free and combined) the paper is boiled with about 5 per cent. sodium carbonate solution, filtered, washed with hot water, and sulphuric acid added to the filtrate. The rosin thus separated is extracted with ether and estimated.

Casein Size.

Casein, usually in the form of ammonium caseate, is used with size in a few mills, in order to give a better "feel" and increased hardness to the paper.¹ It is also used in the preparation of coated papers as an adhesive for the coating material.

For the detection of casein the best reaction is that due to Adamkiewicz. When casein is added to a mixture of 1 vol. of concentrated sulphuric acid and 2 vols. of acetic acid, and warmed, the solution turns a fine red-violet colour; gelatin does not give this reaction.

The extraction of casein from paper is effected by treatment with a

¹ Cf. Hofman, *Handbuch der Papierfabrikation*, p. 380.

solution of borax or of dilute alkali, and then separating it from the solution by acidifying, and when necessary, by warming with acetic acid.

The separated albuminoids are filtered off, dried, and tested for in the manner described above. If, with small quantities of proteids (albuminoids), no precipitation results, the whole of the solution is evaporated to dryness, and the residue tested. Sometimes such a deep yellow coloration is formed in applying this reaction that the violet coloration is masked.

Starch.

Starch sizing, which is no longer in general use in this country, dates back further than animal and vegetable sizing; it has been found in the papyrus of the ancient Egyptians, and even further back, as in the products of the Arabian papermakers.

J. Wiesner¹ has proved that all the sheets of papyrus of the Archduke Rainer used for writing purposes, were sized exclusively with starch. Towards the end of the fourteenth century, animal size came into use, and rosin at the commencement of the nineteenth century; from this date the use of starch as a sizing agent has gradually become less important. It is still used, however, for different purposes, although the views as to its efficiency vary considerably. It serves as an improvement to the sizing effect, retains the loading better, acts as a filler, and gives a finish; for improving the closeness and hardness of the sheet it is usually applied in the form of paste, and also as dry raw starch. Potato starch, on account of its cheapness, is commonly used.

A very dilute solution of iodine is used for the detection of starch in paper. If a drop of iodine solution is put upon a paper containing starch, a blue to violet coloration takes place owing to the formation of iodide of starch. The iodine solution must be very dilute, or else the blue coloration of the paper is hidden by the brown colour of the solution.

For the quantitative determination of the starch present, the paper is treated either with diastase or dilute acid, whereby the starch is converted into sugar, which is determined by any of the usual methods.

Viscose.

Viscose, a cellulose xanthogenate, prepared by the treatment of cellulose with alkali and carbon bisulphide, is to be recommended as an additional sizing agent to rosin, and has already found considerable application. It should give a better sizing property, hardness, and "feel." As an essential sizing agent, that is, in its ink- and water-resisting properties, it is of practically little value, even if used in

¹ *Mitt. a. d. Sammlung des Papyrus Erzherzog Rainer*, 1887, p. 45; *J. Soc. Chem. Ind.*, 1888, 7, 515.

considerable quantities for the purposes above mentioned. Its application is limited to wrapping papers and papers of a similar class; it cannot be used in the manufacture of white papers, owing to its colour. The detection of the presence of viscose necessitates a very thorough examination.

Klemm¹ makes use of photomicrography for detecting the presence of viscose. According to his observations, the fibres are surrounded by a network of fibrillæ, which take on a colour of grey to brown shading in iodine solution, and a violet with chlor-zinc iodine solution.

Wax, Paraffin, Stearine, Fat, Oil.

These substances are employed in making special classes of paper (copying papers, paraffin papers, etc.), partly as an addition to the pulp, and partly by impregnating the finished sheet.

For their detection large quantities of the paper are extracted in a Soxhlet apparatus with ether, chloroform, or other solvents, the solution evaporated upon the water-bath, and the residue examined for its chemical properties. (Iodine value, saponification value, etc.)

THE DETERMINATION OF THE RATE OF FILTRATION AND SEPARATING CAPACITY OF FILTERING PAPER.

Rate of Filtration.—For a consideration of the value of filter paper the velocity with which it filters liquids is a most important factor; that is, under equal conditions, the more rapidly the paper filters the greater is its value. This property can be expressed numerically by determining the time of flow of a certain quantity of water through a fixed surface area of paper under a constant pressure. The determination is carried out in such a manner that the filter, which is of a definite size, is put into a funnel of a certain angle, and a definite quantity of water poured upon it. The experimental conditions are not always identical while this is going on. The filtering surface is not always equally large, the water pressure varies, and moreover the results may be influenced by incidental circumstances, such as absorption.

In the Herzberg (Fig. 91) filtering apparatus,² which is based on Marriott's principle, these sources of errors are avoided. The quantity of water is determined which flows through a surface of 100 sq. cm. in one minute under a water pressure of 50 mm., the temperature of the water being 20°.

In order to ascertain the rate of filtration of various filter papers which are on the market, thirty different kinds were tested. The

¹ *Handbuch der Papierkunde*, p. 255.

² *Papierprüfung*, 3rd edition, p. 130.

quantity of water which passed through in one minute was found to vary from 23-760 c.c. The variations within these limits were as follows :—

0 to 100 c.c. 4 papers	101 to 200 c.c. 3 papers	201 to 300 c.c. 7 papers	301 to 400 c.c. 4 papers	401 to 500 c.c. 3 papers	501 to 600 c.c. 3 papers	601 to 700 c.c. 4 papers	701 to 800 c.c. 2 papers
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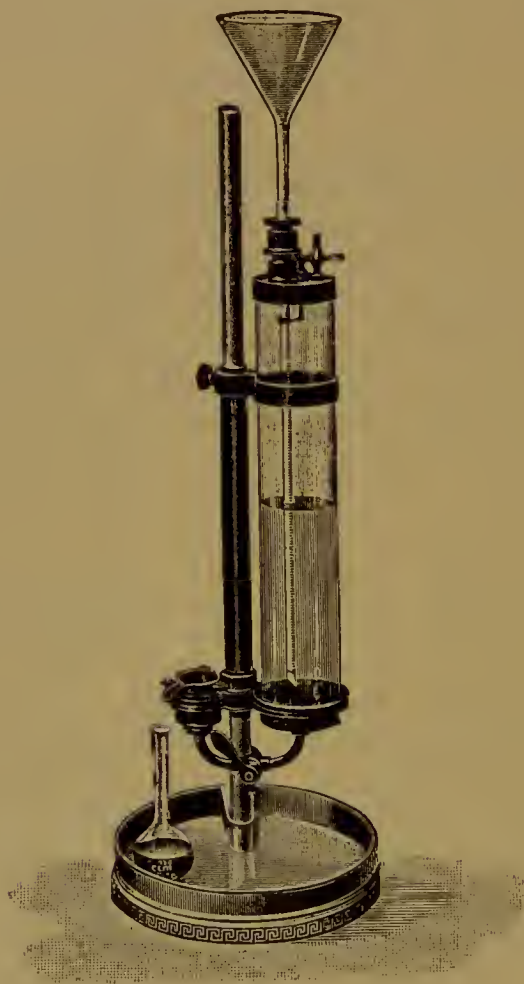


FIG. 91.

Separating Capacity.—A second important property of filter paper is its separating capacity, *i.e.*, the property that the paper possesses of retaining more or less completely suspended matter such as precipitates, etc., from solutions.

In order to get an idea of the value of filter paper for chemical work, it is convenient to test it with a barium sulphate precipitate in the following manner :—Two separate portions of equal parts of barium chloride solution (122 g. per litre of water) and potassium sulphate solution (87 g. per litre of water) are mixed together, one hot and the other cold. The hot mixture, after precipitation, is filtered hot, the cold mixture in the cold, through a round filter paper cut to a diameter of

about 10 cm., and fitted into a smooth funnel as usual and moistened with water.

Papers with pronounced separating properties give clear filtrates from barium sulphate when precipitated cold; others give a turbid filtrate from the cold solution, but a clear filtrate from the hot precipitation; others again give turbid filtrates in both cases. The treatment of the barium sulphate precipitates should be as far as possible under similar conditions; by vigorously shaking, the precipitate can be so modified that it passes through the filter less freely than without shaking. In judging the value of a filter paper the use to which it is to be put, *e.g.* whether industrial or domestic, should be considered.

The Absorbency of Papers (Cross, Bevan, and Bacon).

In addition to the filtering capacity of papers belonging to the absorbent class, an actual comparison of the absorbency of papers such as would be used for blottings is also required. The medium for testing this absorbency may be either water, in which case the strip test is used, or ink, with which the zone test is used.

This comparison involves two factors, namely, the time and the extent of the absorption, though as a matter of fact the two are correlated, in that for a certain interval of time the rate is always proportional to the extent of the absorption.

The Strip Test.—For this test Klemm has classified papers according to the height of absorption after a period of ten minutes. The strips of paper are cut about 1.5 cm. wide and 15 cm. long, preferably in the machine direction, and are suspended in the manner shown in Fig. 92. When the edges are seen to be perfectly straight the strips are lowered into a vessel

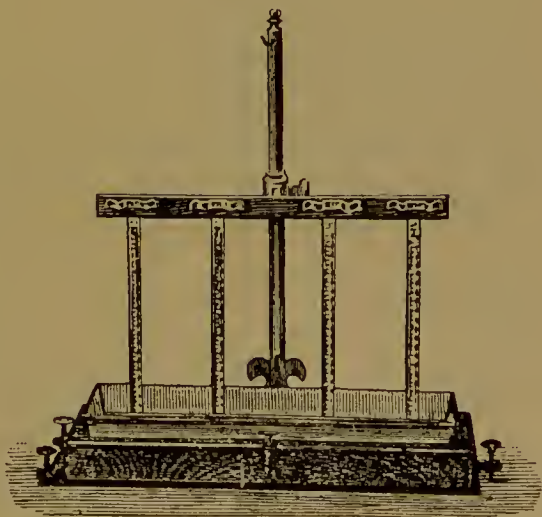


FIG. 92.

containing water to a depth of $\frac{1}{2}$ cm. The water rises rapidly at first but gradually slows down. The following data indicate the character of the results obtained:—

Height of Absorption after Ten Minutes.				Relative Absorbency.
Less than 20 mm.	.	.	.	Very poor
„ 20-40 mm.	.	.	.	Poor
„ 41-60 mm.	.	.	.	Fair
„ 61-90 mm.	.	.	.	Good
More than 90 mm.	.	.	.	Very good

The Zone Test.—This test depends upon the capacity of the paper for filtering out the colouring matter of the ink. If the paper is highly absorbent such filtering out capacity is at a minimum owing to the extremely rapid rate of absorption, whilst in a less absorbent paper the rate of osmosis is much slower, and in this way the crystalloid constituents of the ink, such as water, phenol, etc., are withdrawn from the more colloidal coloured constituents, thus causing the zones to be very much more marked. At the same time, for a given quantity of ink (0.5 c.c.), the circle formed by the ink blot is very much larger in the more highly absorbent paper.

The Imperviousness of Paper to Air (Cross, Bevan, and Bacon).

This property, which is the converse of absorbency and which is possessed to a great extent by parchment papers, is an important one to determine in such papers as Vegetable Parchments, Imitation Parchments, and various wrapping papers, such as Cooking bag papers, Cutlery papers, etc.

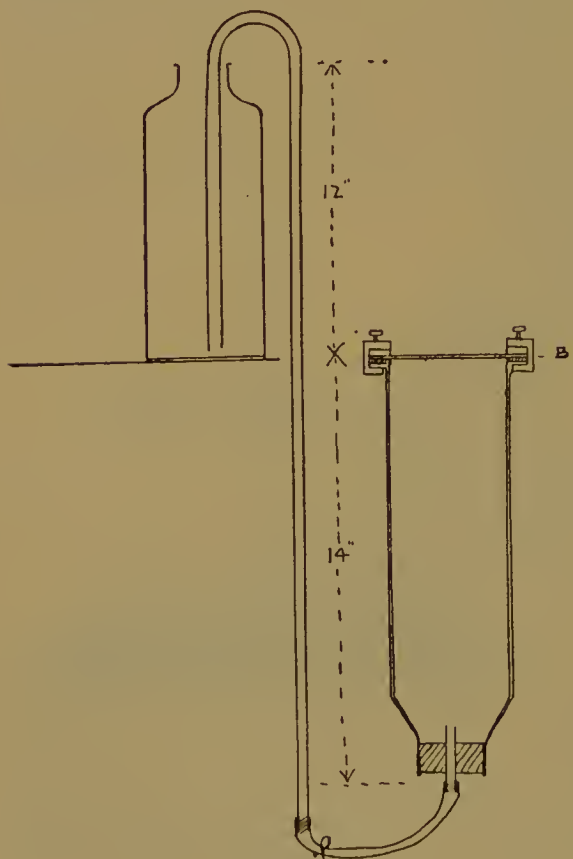


FIG. 93.

A simple method of measuring the resistance of a paper to the passage of air through the pores is as follows:—A circular piece of the paper is suitably clamped on the top of an inverted cylinder, as shown in Fig. 93, the joint being made air-tight by a rubber ring. From a large bottle placed at a suitable height above the cylinder, a stream of water is allowed to flow upwards, and a careful note made of the number of minutes required to drive out the air through the paper. In the case of sound vegetable parchments, it will be found

that the air cannot be forced through the paper by the pressure of the water. The imperviousness of imitation parchments will be found to vary considerably.

THE DETECTION OF FREE CHLORINE AND OF FREE ACID.

It is rarely that papers are found to contain free chlorine or free acid. The method of manufacture more or less precludes the presence of chlorine or of acid in paper. Excess of chlorine from the bleaching of the "half stuff" is rendered inactive by the addition of an anti-chlor, and the large quantities of water with which the fibre comes into contact. Any acid which may have been added in the bleaching operation, or may have been derived from the alum or sulphite cellulose, is partly fixed and partly removed by the washing process.

To test for free chlorine in "half stuff," a small quantity of the material is taken out of the Hollander and, after squeezing, a few drops of potassium iodide starch solution are dropped on; if free chlorine is present a more or less blue colour of iodide of starch is seen.

The test upon the finished paper is best carried out by cutting the paper into pieces, moistening with distilled water, and pressing it between starch iodide paper with a glass plate. The water gradually dissolves any chlorine compounds that may be present, and the chlorine water reacts with the sensitive paper, producing more or less marked blue stripes and spots.

To examine for free acid, as large a quantity as possible of the paper is cut into small pieces and warmed at a moderate temperature in a beaker for about an hour with a minimum quantity of distilled water, stirring frequently. This treatment ensures the solution of practically all the compounds soluble in water, together with any free acid; unusually hard-sized papers retain the last traces of acid. The extract thus obtained is poured off and examined.

The reagent which ordinarily serves as the test for free acid, namely, blue litmus solution, or blue litmus paper, is not applicable in this case, as the extract usually contains aluminium salts which redden blue litmus. The use of Congo red is, however, admissible, as its colour is not changed in the same manner by aluminium salts as it is by free acid. A piece of Congo red paper (prepared by immersing filter paper in a hot, dilute aqueous solution of Congo red) when placed in the extract prepared as above, turns a more or less pure *blue* colour if free acid be present; a dark *violet* coloration may be due to alum. A dilute solution of Congo red may be used directly upon the paper. The sensitiveness of the colour change with Congo red is considerably less than that with litmus, and the reaction is accordingly not always satisfactory. In such doubtful cases the aqueous extract is titrated with a standard solution of potassium hydroxide, using tropæolin as indicator.

For the estimation of free *sulphurous acid* in paper Stockmeier

recommends boiling 50 g. of the paper in a distilling apparatus with water, leading the distillate into a solution of iodine in potassium iodide, and precipitating the sulphuric acid so formed with barium chloride.

Parchment Papers are frequently found to contain acid. Papers of this class have repeatedly been met with, which, as a result of their containing free sulphuric acid, were so tender and brittle that they could not be folded together, the sheets breaking at the least attempt to fold them; when moistened with Congo red solution these papers turned blue at once. The content of acid calculated as sulphuric acid (H_2SO_4), as determined by the titration of the aqueous extract, was found to vary from 0.17-0.57 per cent.

Well-washed parchment papers should contain, at the most, only traces of free acid.

IMPURITIES IN PAPERS INJURIOUS TO METALS.

Papers which are used for wrapping metals, as, for example, sewing needles, knives, leaf metal, etc., must be free from compounds which are capable of attacking metal.

Although it is generally held that paper which is free from chlorine and acid is suitable for wrapping purposes, it is probable that the action upon metals may be due to quite different causes. If silver leaf is attacked by paper used for packing, the cause is usually sulphur or sulphur compounds, derived either from the cellulose or from the anti-chlor; the same paper used for wrapping polished steelware would stand the test excellently, because neither sulphur nor sulphur compounds act readily upon steel. If a paper contains both chlorides and alum, conditions are set up in the presence of moisture which conduce to the formation of hydrochloric acid.¹ In such papers steel goods would rust, but no damage would be done to silver leaf.

The testing of papers intended for the wrapping of cutlery, silver, etc., is best carried out according to the following method of H. Stockmeier:²—Imitation gold leaf, silver leaf, steel plates, etc., are packed up with the paper under examination, and kept for a long time in moist air, both at the ordinary temperature, and at about 50°. If the metals show no change, the papers may be considered technically free from compounds which attack the metals in question. In order to be certain that no external influences have had any action upon the metal, a blank experiment with pure filter paper is carried out at the same time.

¹ Cf. Wurster, *Papier-Zeit.*, 1888, 13, 411; *J. Soc. Chem. Ind.*, 1888, 7, 338. Cf. also P. Klemm, *Wochenbl. f. Papierfabr.*, 1909, 40, 1675; *J. Soc. Chem. Ind.*, 1909, 28, 742.

² *Papier-Zeit.*, 1892, p. 2557.

LOSS OF COLOUR IN PAPER.

The loss of colour on storing is observed in practically all papers in large or small bulk, and after more or less long periods of time, it being brought about specially by the action of light, air, and heat; if heat and light are excluded and the paper is stored in a cool place, no change will occur even after a long time. Papers with lignified fibres turn yellow most easily, as is well known, and most of all, papers containing mechanical wood. It is noticed that such papers have only to be exposed for a very short time to the sun's rays, when a yellowing occurs, the reversion in colour being proportional to the extent of lignification.

Papers free from wood and made without the addition of any colouring matter frequently turn a rather strong yellow colour, which according to the researches of Klemm is due to compounds of iron soap with rosin and fatty substances. The quantity of these compounds is a measure of the tendency to reversion of colour.

For the extraction of these soaps from paper, Klemm recommends a mixture of 2 parts of ether and 1 part of alcohol, and proceeds as follows:—3 g. of the paper are extracted in a Soxhlet apparatus with the ether-alcohol mixture, and the amount of iron determined in the extract by evaporating to dryness, igniting, and taking up the residue with acid. The content of iron is then determined colorimetrically with a mixture of a solution of ammonium thiocyanate and a standard solution of iron chloride or iron ammonium alum. This method is fully described in Vol. I., p. 381.

The determination permits of an accuracy within 0.000001 g. of iron when 5 c.c. of the extract are used for the examination. The total quantity of iron present should not be more than 0.00002 g. If more iron be present in the extract, and it has first of all been so prepared that 5 c.c. corresponds to 1 g. of the paper, the extract must either be correspondingly diluted, or the iron determined by another method.

The content of iron in the form of iron soaps in paper varies between 0.0002 g. and 0.01 g. in 100 g. of paper, or from 0.2 g. to 10 g. in 100 kg.

The reversion of colour due to the action of light is best determined by actual experiment. The carrying out of such tests, however, especially in winter, takes a long time. Artificial light does not yield as definite results as sunlight.

OTHER PHYSICAL PROPERTIES OF PAPER OF IMPORTANCE IN
PAPER TESTING (Cross, Bevan, and Bacon).

The physical properties of paper, apart from those already dealt with, embrace such factors as Opacity, Bulk, Surface, Tenacity, Elasticity, and Strength.

Opacity.

This factor is purely comparative. Any desired paper may be taken as the standard of comparison, and the opacity is usually measured in terms of the thickness of paper required to obliterate rays of light at a certain fixed distance from the paper.

A simple method of comparison is to paste a black cross of paper upon glass, and to fix the latter in a clamp in a darkened room about 30 cm. away from an electric light. It is then easy to press the varying thicknesses of paper up against the glass until the outline of the black cross cannot be seen.

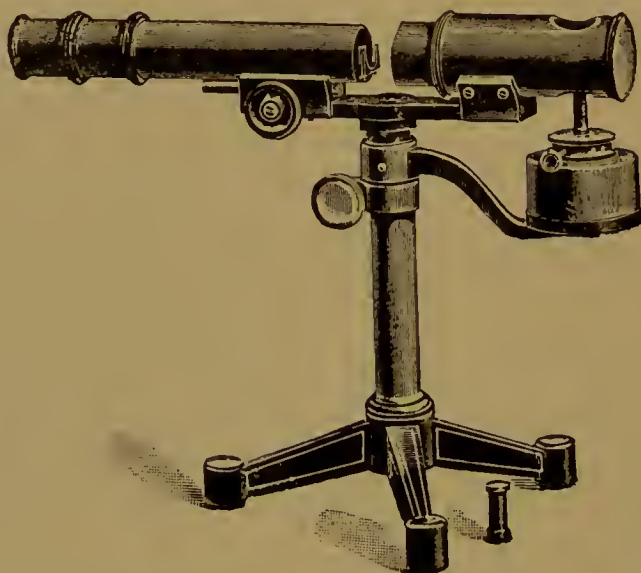


FIG. 94.

A more delicate method is that devised by Klemm, who uses a Hefner-Altenack amyl acetate lamp as the source of illumination. This lamp burning with a definite height of flame gives an illumination equal to one candle, and is fitted into a tube as shown in Fig. 94. Between the cylinder and the tube is a bracket which permits of increasing thicknesses of paper being inserted until the flame is quite obliterated. The relative opacity is obtained by dividing the weight in grams per square metre of the paper into the number of thicknesses of paper required.

Bulk.

This factor is an important one, in that it indicates whether the fibres constituting the web are loosely felted together with a correspondingly large air space, as, for example, in an "antique" or "blotting"; or whether they are closely felted together, forming a compact sheet, as in "banks," "loans," etc. It is expressed by the ratio of the total volume of paper to the volume of fibre. The volume of paper is obtained by any

suitable means, and the volume of fibre in the same units by dividing the weight by 1.5. If any loading is present in the paper this must be determined, not because of the actual influence of the mineral upon bulk, but in order that the weight of loading present may be deducted from the weight of fibre. It is assumed that the mineral occupies a space in the sheet which would otherwise have been occupied by air, and to a certain extent this is true; but it must, however, be borne in mind that the greater the amount of loading, the more open will the sheet be.

Surface.

The extent of finish is frequently of the utmost importance, especially in papers used for half-tone block printing. There is no definite method, however, by which the "surface" can be measured with any degree of accuracy. A simple method for comparing the "surfaces" of papers is to place a glass weight upon the paper while resting upon an inclined plane, and noting the point at which the weight begins to slide. A fair approximation can in this way be obtained, and the measurements recorded either in the sines of the angle as made by the perpendicular and the hypotenuse, or the actual height in any specific units of measurement. The extent of "surface" will be the inverse of the numbers obtained.

Tenacity.

This is measured roughly by the resistance a paper offers to the crumpling test, or more exactly by the loss of strength the paper undergoes after a given number of folds. The determination is made by crumpling a piece of paper about 10 cm. square between the fingers, the four corners of the paper being pulled over to the centre and crumpled between the fingers. It is then opened up, and the four corners again brought to the centre, the paper, however, being reversed. This operation is repeated for any given number of times, or until pinholes can be distinctly seen in the paper when submitted to transmitted light. A more exact determination is carried out by folding in the "machine" direction a given number of times, usually about fifty, and then in the cross direction. A comparison of the breaking strain of the paper so folded, with the original breaking strain, gives an exact measure of the tenacity.

There are special instruments for determining this factor, but it suffices to carefully reverse the fold in exactly the same place each time, and then to test in the breaking strain machine.

Elasticity.

Elasticity, so far as it is measured by the elongation under tensile strains, appears to depend on the same factors as the tensile strength.

Up to certain limits the elasticity is favourably affected by increased hydration of the pulp, but when the gelatinisation is pushed to an extreme limit at the expense of the length of fibre, as in imitation parchment papers, the tendency is to brittleness. Generally speaking, the greater the tensile strength of a paper the greater is the elongation under the breaking strain, though this rule is influenced to some extent by the nature of the fibres. At the same time it is to be noticed that when, as is nearly always the case, a sheet of paper is stronger in one direction than in another, the direction of the greatest strength is the direction of least elongation, and *vice versa*. This depends on the relation and disposal of the fibres being more definite in one direction than in the other.

Breaking Weight and Bursting Strain.

The resistance of paper to fracture can be measured by various methods. One of the best is the *Dead-Weight Method*, in which strips of paper of a definite width are cut parallel to and at right angles to the machine direction. A strip is clamped at both ends and subjected to a gradually increasing strain until it is broken. Three or more tests should be made in each direction with strips taken from different parts of the sheet; the mean result represents the average strength of the paper. The machine made by Schopper¹ is one of the best for this test.

Another method, similar in character, is the *Spring System*. The force is applied in the same way, namely, by a handle attached to a spring fixed to a dial which indicates the strain in pounds.

A third system which is quite different in principle, is the *Bursting Strain Machine*, where the paper is subjected to a strain acting in all directions which is constantly increased until rupture occurs. This factor is very useful, as it does away with the necessity of the careful cutting of the strips required by the other systems, and though perhaps it does not permit of similar standardisation, it provides a very rapid and accurate means of comparing the strength of various papers.

The following classification of papers has been adopted in Germany.

Class.	1.	2.	3.	4.	5.	6.
(a) Mean breaking length (metres) not less than .	6000	5000	4000	3000	2000	1000
(b) Mean elongation (per cent.) at fracture not less than	4.5	4.0	3.0	2.5	2.0	1.5
(c) Resistance to rubbing.	6.0	6.0	5.0	4.0	3.0	1.0

¹ L. Schopper, Arndtstrasse 27, Leipzig.

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TEXTILE FIBRES

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I. THE MORE IMPORTANT REAGENTS AND OPERATIONS EMPLOYED IN THE TESTING OF TEXTILE FIBRES.

THE concentrations, etc., of the reagents used must be very carefully adhered to, as otherwise the results obtained will not be reliable.

(1) *Iodine Solution and Sulphuric Acid Mixture.*—(a) The iodine solution is prepared by dissolving 1 g. of potassium iodide in 100 g. of distilled water, and then adding iodine until the solution is saturated, *i.e.*, until undissolved iodine separates. The excess of iodine is allowed to remain in the solution, so that the liquid may be kept in a constant state of saturation. The iodine solution must, however, be renewed from time to time. C. Hartwich recommends a solution containing 3 parts KI, 1 part I, and 60 parts H_2O .

(b) The sulphuric acid mixture. To a mixture of 2 vols. of purest glycerol and 1 vol. of distilled water are added very gradually and carefully, and with constant cooling, 3 vols. of concentrated sulphuric acid. In order to keep this mixture in the correct state of concentration, a small quantity of concentrated sulphuric acid is added from time to time.

Both the above reagents are used together for the analysis of cellulose (vegetable fibres) and for lignified fibres.

The fibres, or their cross-sections, are placed on a microscope slide, and a few drops of the iodine solution are added. After allowing to act for some time, the excess of the solution not absorbed by the fibres is removed carefully by means of filter paper, and 1-2 drops of the sulphuric acid mixture are added. Pure cellulose does not swell and is coloured a pure blue, whilst lignified fibres are coloured yellow.

The efficiency of the two reagents may be readily tested, according

to Höhnel, by treating several linen fibres in the manner described above. On addition of sulphuric acid the fibres must not swell, and they must be of a pure blue colour. If the fibres swell, the sulphuric acid is too concentrated; but if the blue colour appears but slowly or, if the shade is more of a violet or pink, the sulphuric acid is too dilute. In the former case a little glycerol, in the latter a small quantity of sulphuric acid, must be added.

(2) *Zinc Chloride Iodine Solution* may be used in place of the iodine solution and sulphuric acid mixture. This solution colours cellulose reddish- to blue-violet. It is prepared by adding a concentrated solution of zinc chloride to an aqueous solution of iodine in potassium iodide. According to Hartwich the solution should contain 8 parts KI, 25 parts ZnCl_2 , and 8.5 parts water, and sufficient iodine to keep it saturated.

(3) *Reagents used for the Identification of Lignified Fibres.*—The following well-known reagents are used:—(a) An aqueous solution of indol and hydrochloric acid (red coloration); (b) aniline sulphate or hydrochloride with (although not absolutely necessary but very useful) an addition of dilute sulphuric acid (golden yellow colour); (c) phloroglucinol (in a 10 per cent. alcoholic solution) and concentrated hydrochloric acid (red coloration); (d) α -naphthylamine hydrochloride (orange coloration).

It should be stated that cross-sections of jute do not give the colour reactions with most of the reagents given under (3), whilst they always give the yellow coloration when treated with iodine and sulphuric acid.

From the observations of Hartwich,¹ jute gives the lignin reaction with phloroglucinol and hydrochloric acid (red), and with zinc chloride iodine (violet).

Jute, from which the lignin has been removed by artificial means, may, however, be met with.

As a test for lignin E. Nickel² recommends hydrazine sulphate and phenylhydrazine hydrochloride. A cold solution of hydrazine sulphate produces in a few minutes a distinct light yellow coloration on wood. If, after the yellow colour has fully developed, a 20 per cent. solution of hydrochloric acid is applied, the yellow changes to orange, which gradually increases in intensity.

With a solution of phenylhydrazine hydrochloride wood becomes faintly yellow coloured; the colour becomes stronger on addition of dilute hydrochloric acid (about 15 per cent.). If the treated wood is left, in the course of an hour or so (with many kinds of wood a considerably longer time is required), the yellow colour changes to a fairly pure green.

¹ Private communication to Prof. Gnehm.

² *Chem. Zeit.*, 1893, **17**, 1209, 1243; *J. Soc. Chem. Ind.*, 1893, **12**, 869.

(4) *Ammoniacal Cupric Oxide*.—This solution will only give the characteristic reactions if carefully prepared according to the following instructions (Höhnelt):—(a) To a solution of copper sulphate, ammonia is added. The blue precipitate produced is collected on a filter, well washed, and then freed, as far as possible, from excess of liquid by pressing between filter paper. The moist precipitate is then dissolved in the smallest possible quantity of concentrated ammonia; or (b) copper sulphate is precipitated with a dilute solution of sodium hydroxide; the precipitate is well washed with water and dissolved in 20 per cent. ammonia.

The resulting dark blue liquid, which smells strongly of ammonia, should be kept in the dark in a well-stoppered bottle. When properly prepared, the solution dissolves dry cotton readily. Fibres consisting of pure cellulose or those which have been previously freed from lignin by treatment with nitric acid, or fibres which are only slightly lignified (*e.g.* hemp), either swell strongly or dissolve, in a good solution of ammoniacal cupric oxide. Highly lignified fibres are not attacked or swell only very little.

If the freshly prepared reagent dissolves cellulose very rapidly, so that it is impossible to observe the swelling of the fibres under the microscope, it is best to first immerse the fibres in water, and to remove the excess of water before treating with the reagent.

(5) *Ammoniacal Nickel Solution*.—A solution of 25 g. of nickel sulphate (crystals) in 500 c.c. of water is precipitated with sodium hydroxide. The precipitate is well washed and dissolved in 125 c.c. of concentrated ammonia and 125 c.c. of water.

This solution dissolves silk rapidly; linen and cotton when treated with it lose only 0.45 per cent. and pure wool 0.33 per cent. in weight.

(6) *The Separation of Fibre Bundles into Ultimate Fibres*.—This is necessary when single fibres have to be examined, and is effected by boiling with Schulze's mixture.

According to Hartwich, the following method is used:—Place the fibres in a test tube, add a few cubic centimetres of nitric acid and a small quantity of potassium chlorate, heat to the boil and allow to stand until no more effervescence takes place; then wash the material with water and disintegrate on a microscope slide. Boiling must not be continued beyond a certain time, because otherwise many of the fibre bundles would already become disintegrated in the test tube.

Vétillard's method consists in boiling the fibres in a 10 per cent. sodium carbonate solution. They are then thoroughly washed and rubbed between the fingers in order to complete the separation. The method is indispensable when it is a question of preserving the lignin in the fibres, although the operation is frequently a lengthy one, the boiling occupying days.

(7) *The Preparation of Thin Cross-Sections.*—According to Höhnel, these are prepared as follows:—After placing a small bundle of fibres as parallel as possible, impregnate and then cover with a strong solution of gum containing glycerol, and allow to dry. If too much glycerol is present the fibre bundle will remain too soft, whilst if too little glycerol has been used the bundle will become brittle on drying and will break during the cutting of the cross-section.

According to Hartwich, the mixture should be prepared as follows:—Slowly dissolve 70 g. of gum arabic in 70 c.c. of water; allow 4 g. of isinglass to swell in 16 c.c. of warm water and then press through muslin. Mix 10 g. of the latter with the gum solution and warm the whole on the water-bath with the addition of 12 g. of glycerol.

The dried fibre bundle is laid between two corks which are then clamped firmly and bound together. By using a sharp razor, cross-sections of a convenient thickness can be obtained; these should, as nearly as possibly, be cut at right angles to the axis of the fibre.

When cutting the fibres, no attempt should be made to obtain cross-sections through the whole bundle at a time, but to cut off a number of small, very thin pieces. The sections are then placed on a microscopic slide, with a very small drop of water. With a large drop of water the sections become too much scattered, and they are then difficult to locate.

II. THE CHEMICAL EXAMINATION OF TEXTILE FIBRES.

The behaviour of the fibres towards the different reagents will be seen from the following Tables.¹

1. Characteristic Colorations with Dyestuffs.

	Wool.	Silk.	Flax.	Cotton.
Madder extract . . .	Not coloured Scarlet; little affected by bleaching powder solution	Not coloured Scarlet; little affected by bleaching powder solution	Orange Violet; slowly discharged by bleaching powder solution	Yellow Light red; quickly discharged by bleaching powder solution
Cochineal				
Magenta solution (accord- ing to Liebermann ²)	Red	Red	Not coloured	Not coloured
Acid dyestuffs . . .	Dyed	Dyed	Colourless	Colourless
Mikado dyestuffs	Dyed	Dyed

¹ Herzfeld, *Die techn. Prüfung d. Garne, u.s.w.*, 1896.

² To a saturated solution of magenta, sodium hydroxide is added drop by drop, until discoloration takes place.

2. Action of Solutions of Different Salts.

	Wool.	Silk.	Cotton and Flax.
Zinc chloride ¹ . .	Partially dissolved	Dissolved	Not dissolved ; violet coloration
Stannic chloride . .	No change	No change	Black
Silver nitrate . . .	Violet to brownish-black	No coloration	No action
Mercuric and mercurous nitrate (Millon's reagent)	Brick-red to brown	Do.	Do.
Sulphate of copper or iron	Black	Do.	Do.
Plumbite of soda (alkaline lead solution)	Black	Do.	Do.
Ammoniacal cupric oxide	Swelling only	No action	Swells and dissolves, with blue coloration
- - Do. nickel oxide.	Not dissolved	Dissolves	Not dissolved

3. Action of Alkaline Solutions.

	Wool.	Silk.	Flax.	Cotton.	Hemp.	Jute.
Potassium hy-droxide	Dissolves	Dissolves	Swells fibres, becomes brown and yellow, fading later	Swells fibres, tinted a weak yellow	Fibres brown	Fibres brown
Sodium hy-droxide	Do.	Dissolves slowly and tinted reddish	Brownish-yellow	Weak yellow	Brownish	Brownish
Ammonia	Before retting : orange-yellow ; retted : light violet	...

	Wool.	Silk.
To the alkaline solution of the fibre is added :		
(a) Sodium nitroprusside . .	Violet	No change
(b) Lead acetate solution . .	Turns blackish	...
(c) Copper sulphate . . .	Violet, later brown	Violet

Detection of lignin in hemp, jute, etc. : aniline sulphate—yellow ; indol and sulphuric acid—pink ; α -naphthylamine hydrochloride—orange ; phloroglucinol—red.

¹ Concentrated solution of sp. gr. 1.7.

4. Action of Acids, etc.

	Wool.	Silk.	Flax.	Cotton.	Hemp.	Jute.
Sulphuric acid	Dissolves only on heating	In hot acid quickly dissolved	Dissolved in cold concentrated acid	Quickly dissolved	Slowly dissolved	Slowly dissolved
Nitric acid	Yellow coloured, dissolves slowly	Yellow coloured, dissolved slowly	Not dyed, dissolved	Not dyed	Yellowish	...
Chlorine water	Becomes brittle and yellow	Becomes yellower	Bleached	Bleached	Yellowish-brown	Becomes violet on addition of ammonia
Iodine solution	Yellowish-brown to yellow	Yellow	...	Light brown
Picric acid	Yellow	Yellow
Iodine and sulphuric acid (cellulose reaction)	Swells, blue coloration	Swells, blue coloration	Swells slowly, greenish coloration	Swells slowly, yellow to brown coloration
Thymol and sulphuric acid (cellulose reaction)	Reddish-violet	Reddish-violet
Sugar and sulphuric acid (furfural reaction)	Rose-red	Rose-red

F. J. G. Beltzer¹ applies a solution of "Ruthenium red" ($\text{Ru}_2(\text{OH})_2\text{Cl}_4(\text{NH}_3) + 3\text{H}_2\text{O}$, 0.01 g. in 10 c.c. of water) for the characterisation of textile fibres. Pure normal cellulose is not stained, oxycelluloses, pectins, gums, and mucilages are stained, whilst lignified tissues, either fresh or preserved in alcohol, are not stained; after treatment with alkalis or sodium hypochlorite they are coloured a bright pink. Raw cotton is coloured a faint pink; raw flax, ramie, hemp, and jute are strongly but irregularly coloured. Both wood cellulose and raw wood fibres are coloured irregularly, and whilst bleached jute is strongly coloured, raw kapok fibres remain practically colourless.

When testing fibres which have undergone a chemical treatment, any trace of acid present must be removed by washing with alkaline water.

Wool is not stained, and silk only slightly, after twelve hours' immersion in the solution.

The different kinds of artificial silk can also be identified by means

¹ *Monit. Scient.*, 1911, 1, 633; *J. Soc. Chem. Ind.*, 1911, 30, 1206.

of Ruthenium red. Denitrated collodion silk is coloured a deep red; cuprammonium silk, prepared from cotton, is scarcely stained, whilst viscose silk, prepared from wood cellulose, is coloured a deep pink. Collodion silk which has not been denitrated remains colourless, whilst acetate silk is irregularly stained.

A.—Methods of Distinguishing Animal and Vegetable Fibres.

1. *H. Molisch's Method*.¹—About 0.01 g. of the previously well-boiled and washed fibres (in order to remove finishing materials, etc.) are placed in a test tube with about 1 c.c. of water; 2 drops of a 15-20 per cent. alcoholic solution of α -naphthol and finally concentrated sulphuric acid (approximately as much as the total volume of the solution) are then added. The liquid when shaken in the presence of vegetable fibres immediately becomes a deep violet and the fibres dissolve, whilst with fibres of animal origin the liquid becomes only more or less yellowish to reddish-brown.

If thymol is used, a beautiful vermilion or carmine colour is produced, the latter especially if the solution is diluted with water.

If at the same time the solubility or insolubility of the fibres is taken into consideration, this will give an indication as to whether a fabric consists only of vegetable or animal fibres, or of a mixture of both, or of silk.

If the material either does not give the α -naphthol reaction, or only very slightly, or if the reaction is not permanent as is the case with silk:—

- | | | |
|---|---|---------------|
| (1) The fabric dissolves immediately and completely | . | Silk |
| The fabric does not dissolve | . | Wool |
| The fabric dissolves partially | . | Wool and silk |

If the material gives a brilliant reaction with α -naphthol:—

- | | | |
|--------------------------------------|---|---|
| (2) The fabric dissolves immediately | . | { Either pure vegetable fibres
or mixed with silk. |
| The fabric dissolves partially | . | { Vegetable fibres and wool,
and possibly also silk. |

It is immaterial whether the fibres are dyed or undyed, because dyestuffs do not interfere with the reaction.

2. *The Behaviour of Fibres towards an 8 per cent. Solution of Sodium or Potassium Hydroxide* (sp. gr. 1.04-1.05) may also be considered as a reliable test. Animal fibres, on boiling with this solution, are completely dissolved, whilst vegetable fibres are only very slightly attacked.

3. *The Rosaniline Reaction*.²—This reaction is chiefly used in order

¹ *Dingl. polyt. J.*, 1886, 261, 135; *J. Soc. Chem. Ind.*, 1886, 5, 642.

² *Bolley-Stahlschmidts Handb. d. tech.-chem. Untersuchungen*, 5th ed., vol. ii., p. 857.

to distinguish between cotton and wool. The colourless rosaniline solution is prepared by dissolving magenta in boiling water, and whilst boiling, sodium hydroxide or ammonia is added, drop by drop, until the colour has disappeared. The filtered solution, from which small crystals of rosaniline separate on cooling, may be kept in a stoppered bottle for an indefinite period.

If a fabric consisting of wool and cotton is immersed in the hot or boiling solution to which a small quantity of ammonia has been added, for a few seconds, it frequently remains colourless; but on washing with water until free from alkali, the wool is coloured red whilst the cotton remains colourless. Silk behaves like wool; linen and other vegetable fibres like cotton.

4. *Behaviour towards Boiling Nitric Acid.*—Vegetable fibres, especially cotton, flax, and hemp, remain white, whilst wool and silk are coloured yellow, the latter a lighter shade than the former.

5. *Action of a "Nitrating Mixture."*—According to Peltier, the material to be examined is immersed for about a quarter of an hour in a mixture of equal volumes of concentrated nitric acid and concentrated sulphuric acid. It is then well washed. Silk (and also goats' hair) is perfectly dissolved, wool becomes coloured yellow or yellowish-brown, whilst neither the colour nor the structural characteristics of the vegetable fibres are changed. It will be noticed that after drying they have become highly inflammable.

6. *Behaviour of the Fibres during Burning.*—The smoke of burning silk and wool smells like burnt horn. Animal fibres burn much more slowly than vegetable fibres. Moist turmeric paper is turned browner by the smoke from burning animal fibres, whilst moist neutral litmus paper is turned red by the acid vapour from burning vegetable fibres.

Vegetable fibres leave a cinder in the form of the original thread, and on complete combustion a very small quantity of ash.

Animal fibres leave a shining tumified residue which burns with difficulty, and on complete combustion leaves a comparatively large amount of ash.

7. B. Manea¹ has described a quick method for distinguishing vegetable from animal fibres by means of oleic acid and sulphuric acid. Cellulose, starch, vegetable albumin, nitrocellulose, artificial silk, dextrin, sugar, etc., give a characteristic colour reaction on treatment with sulphuric acid with the addition of either free or saponified oleic acid and a little water, which is not produced with either stearic or palmitic acid.

Cotton or any similar material to be examined is dissolved in concentrated sulphuric acid. A small quantity of oleic acid, or an oil containing oleic acid (colza oil) is then added, and water is

¹ *Bull. Soc. d. Stiinte du Bucuresti-Romania*, 1908, 17, 256; *J. Soc. Chem. Ind.*, 1908, 27, 1161.

stirred in, drop by drop, until the appearance of a red coloration which gradually changes to violet. A coloured ring is formed if the solution is not agitated.

Fibres of animal origin do not give this reaction, and it therefore serves as a convenient method for the distinction of artificial from natural silk. If the fabrics to be examined have been finished, it will be advisable to boil first with water, wash and dry. Dyestuffs do not interfere with the reaction.

B.—Methods of Distinguishing Different Fibres from Each Other.

1. *Wool and Silk*.—(a) The fibres are treated with concentrated sulphuric acid. Silk is fairly rapidly dissolved, whilst wool is not attacked. The separation is a quantitative one. After allowing the sulphuric acid to act for a sufficient length of time, dilute strongly with water, filter through a fairly open cloth filter, wash and weigh the dried wool. (b) According to Lassaigne a solution of oxide of lead in sodium hydroxide (sugar of lead treated with sodium hydroxide until the white precipitate formed is re-dissolved) may be used. Treated with this solution moistened silk and vegetable fibres are not coloured, whilst wool and hair are coloured brown. (c) Ammoniacal cupric oxide dissolves silk but not wool. (d) Dissolve the sample in potassium hydroxide, and then add sodium nitroprusside. A violet coloration is produced if wool is present.

2. *Cotton and Linen*.¹—(a) The so-called Kindt's test may be used. White fabrics should be freed, as far as possible, from finishing materials. This is effected by boiling in distilled water followed by rubbing. The re-dried pieces are immersed in concentrated sulphuric acid for one to two minutes, according to the strength of the material, rinsed with water, rubbed between the fingers, and then placed in a dilute solution of ammonia, in order to completely remove any traces of sulphuric acid, and finally dried. The cotton threads are dissolved and are entirely removed by the rubbing. The linen threads remain unaltered or are only slightly attacked. In order to obtain reliable results, it is necessary to completely remove the finishing materials. The result also depends upon the length of time of immersion in the acid.

(b) *Frankenheim and Leykauf's Olive Oil Test*.—The bleached fabric, after having been freed from finishing materials, is dipped in olive oil. The excess of oil is removed by gently pressing between filter paper. The linen fibres appear semi-transparent, like oiled paper, whilst the cotton fibres are not changed. The fabric has a

¹ See also, *Die Unterscheidung von Baumwolle und Leinen*, A. Herzog, 2nd ed., 1908; *Z. Farb. Ind.*, 7, 183, 204, 206; *Chem. Zentr.*, 1908, II., 546.

striped appearance. If placed upon a dark ground, the linen fibres appear dark, the cotton fibres white.

(c) *The Rosolic Acid Test*.¹—Linen treated with an alcoholic solution of rosolic acid, and then with concentrated sodium hydroxide solution, is coloured pink. Cotton is not coloured permanently.

(d) *H. Behrens' Methylene Blue Test*.—The cloth is dyed in a warm solution of methylene blue, and is then thoroughly washed. Repeated washing completely removes the dyestuff from the cotton, whilst the linen fibres remain distinctly coloured. During an earlier stage of the washing, and particularly in artificial light, cotton exhibits a more greenish-blue colour than linen.

A. Herzog² recommends the following method as especially suitable for the examination of half-linen (linen and cotton):—

Cut a square piece (about 4 sq. cm.) from the fabric, remove the outer threads and place it for a few minutes in a lukewarm alcoholic solution of cyanin. Now rinse in water and then treat with dilute sulphuric acid. The colour is completely removed from the cotton, whilst the flax fibres remain distinctly blue. The coloration is due to the dyestuff being fixed upon the remaining parts of the epidermis on the linen fibre, which have a strong affinity for the cyanin. If the fibres after treatment with sulphuric acid and washing are placed in ammonia, the blue coloration of the linen is considerably deepened.

3. T. F. Hanauseck³ has described a new method for distinguishing flax from hemp. If a few flax and hemp fibres are placed in chromic acid (prepared by mixing potassium bichromate with an excess of sulphuric acid), the fibres begin to swell after a few seconds. The originally yellow liquid gradually becomes green in the vicinity of the fibres. By carefully observing the disintegration, particularly as regards the inner cuticle of the fibres, a distinction can be made between flax and hemp.

4. *Jute from Linen and Hemp*.—In practice the question often occurs as to whether a cloth consists of either pure hemp or flax, or whether it also contains jute. The detection of jute by means of its microscopic characteristics is not difficult (unequal thickness of the single bast fibres), but it requires practice and careful examination.

According to W. Lenz,⁴ examination in polarised light greatly facilitates the distinction of these fibres. For this purpose the threads are disintegrated by Schultze's method, viz., by warming with nitric acid to which a trace of potassium chlorate has been added; they are then washed, warmed with alkaline water, and finally strongly shaken with

¹ Elsner, *Die Praxis des Nahrungsmittel-Chemikers*, 3rd ed., p. 267.

² *Z. Fabr.- u. Text.-Chemie*, 1905, p. 11; *J. Soc. Chem. Ind.*, 1906, 25, 338.

³ *Z. Farb. Ind.*, 1908, 7, 105; *J. Soc. Chem. Ind.*, 1908, 27, 400.

⁴ *Z. anal. Chem.*, 1890, 29, 133; *J. Soc. Chem. Ind.*, 1890, 9, 732.

distilled water. The fibres are now placed on the microscopic slide, which is then allowed to remain in a horizontal position until the water has evaporated, when a drop of glycerol is added. The fibres are now

Table for the Examination of all Textile Fibres.

The fibre mixture is treated with a 10 per cent. solution of sodium or potassium hydroxide.

Partially dissolved.			Partially undissolved.			Completely dissolved.					
With zinc chloride solution.											
Com- pletely dissolved	Partially dissolved	None dissolved	Does not dissolve			Dissolves partially		Does not dissolve			
The alkaline solution does not become black on addition of lead acetate : silk	The soluble portion does not become black on addition of lead acetate ; the insoluble portion be- comes black on addition of lead ace- tate : silk and wool	The whole mass be- comes black on addition of lead acetate : wool	Chlorine water or ammonia			Lead acetate		Nitric acid dyes partly yellow ; the other part re- mains white : mixture of flax and cotton			
			Reddish- brown	No coloration		Blackens	Does not blacken				
				The fibre becomes red with fuming nitric acid: New Zealand flax	Alcoholic magenta solu- tions colours the fibre				Potassium hydroxide partly dis- solves the fibres insol- uble in zinc chloride; the re- maining fibres dissolve in ammoni- acal cupric oxide : mix- ture of wool, cotton, silk	Picric acid dyes partly yellow; the other part re- mains white : silk and cotton	
					Permanently						Colour washes out
					Potassium hydroxide dyes yellow						Potassium hydroxide does not dye yellow : cotton
					Iodine and sulphuric acid colour						
Yellow: hemp	Blue: flax										

covered with a cover-glass and examined under the microscope with crossed Nicols (Seibert objective No. 3, magnification about 200). Almost every flax and hemp fibre exhibits a brilliant coloration.

Jute fibres, on the other hand, are more uniformly bluish or yellowish coloured. Only few fibres appear similar to linen, but less brilliantly coloured. The individual fibres should be completely separated. If

fibres cross each other, brilliant coloration will appear at the points of contact. The cross-lines which are more or less at right angles to the cell walls of the bast cells, as well as the remaining particles of parenchymatous tissue, appear much more distinct in polarised than in ordinary light, especially at a magnification of about 600 diam. (Seibert's system No. 5).

According to Hartwich, the examination in polarised light is not always reliable, since the polarisation colours may vary with the position of the fibres. Jute is best distinguished from linen and hemp by means of a solution of phloroglucinol. Jute is immediately coloured red, linen is not affected, hemp only very faintly coloured.

5. *Cotton and Kapok*.—With Schultze's zinc chloride iodine solution cotton gives a blue, kapok a yellow coloration. If the material is placed in a dilute alcoholic solution of magenta (0.01 parts magenta, 30 parts alcohol, 30 parts water) for about one hour at the ordinary temperature, then washed until the wash-water becomes colourless, kapok becomes dyed a brilliant red, whilst cotton remains white.

A quantitative estimation may be carried out by using B. Tollens' method, *i.e.*, distilling with dilute hydrochloric acid and precipitating the furfural formed with phloroglucinol. Kapok contains 23-25 per cent. of pentosans, cotton at most only 3 per cent. The percentage of cotton can, therefore, be readily calculated.¹

Pinchon recommends the method of examination given in the Table on p. 874.

C.—Quantitative Estimation of Individual Fibres in Fibre Mixtures.

1. *Cotton and Wool*.—The estimation of the percentage of cotton in wool is carried out in the following manner, which is the official method adopted by the German Government² (1896). Place 5 g. of the yarn into a beaker glass of 1 litre capacity with 200 c.c. of 10 per cent. sodium hydroxide solution; bring the liquid slowly to the boil (in about twenty minutes) and boil gently for fifteen minutes. By this time the wool has been completely dissolved. Finished woollen yarns must be previously treated with a 3 per cent. solution of hydrochloric acid. The material is then washed until free from acid. After the wool has been dissolved, the liquid is filtered and the residue dried gently. The hygroscopic mass is then allowed to remain in the air for a short time before it is weighed. Hunger³ states that cotton is attacked by 10 per cent. sodium hydroxide solution and that it loses

¹ M. Greshoff, *Pharm. Weekblad*, 1908, 45, 867; *J. Soc. Chem. Ind.*, 1908, 27, 937.

² *Fischer's Jahresber.*, 1898, p. 1103.

³ *Zeits. f. öffentl. Gesundheitspflege*, 1898, p. 160.

4 per cent., and that it also loses 4 per cent. during the treatment with 3 per cent. hydrochloric acid. Yarns which are free from finishing materials can be estimated by this method, but 4 per cent. should be added to the weight of the cotton; finished yarns cannot be estimated correctly by this method.

L. Losseau¹ suggests the following method for the estimation of cotton in wool. A sample of 10-20 g., after drying at 110°, is boiled with a 1-2 per cent. solution of sodium hydroxide for ten minutes. The wool dissolves, whilst the cotton remains intact. After washing and drying at 110°, the weight of the residue represents the cotton contained in the material.

More reliable results than those obtained by the methods given above are, according to B. Ruskowski and E. Schmidt,² obtained by employing the method of S. Kapf,³ which is used in the public Conditioning House in Aix-la-Chapelle. The material to be examined is first freed from oil and fat by treatment with ether, carbon bisulphide, or other similar solvent. It is then treated with a 2 per cent. solution of hydrochloric acid for fifteen minutes, in order to remove any finishing materials present, then thoroughly washed and dried at 110°. The dried material, after weighing, is boiled in a 2 per cent. sodium hydroxide solution for fifteen minutes. The water which evaporates must be replaced by adding distilled water. The remaining cotton is first washed with water, then with dilute acid, and finally with water, and dried. The residue is weighed, and from this the percentage of cotton and wool present in the material can be calculated by taking two constants which have been ascertained by experiment. Cotton loses by boiling in sodium hydroxide solution 3.5 per cent. Washed wool by extraction with water loses about 1 per cent. It should, however, be pointed out that losses may occur due purely to mechanical action⁴ (fibre dust in drying, etc.).

A practical method by B. Ruskowski and E. Schmidt⁵ is based upon the nitrogen-content of wool.⁶ The estimation of nitrogen in a series of different kinds of wool by Kjeldahl's method gave a mean value of 14.002 per cent. N. The sample is first freed from fat in the usual

¹ *Fischer's Jahresber.*, 1898, p. 1107.

² *Chem. Zeit.*, 1909, 33, 949; *J. Soc. Chem. Ind.*, 1909, 28, 1030.

³ *M. Textil*, 1898, p. 153; *J. Soc. Chem. Ind.*, 1898, 17, 956; *Textil Zeit.*, 1900, p. 462.

⁴ See also, A. Pinagel, *Chem. Zeit. Rep.*, 1909, 31, 339, 449; Heinisch, *Brünner Monatsschrift f. Text.-Ind.*, 1908, 15, 330; *Chem. Zeit. Rep.*, 1908, 32, 619.

⁵ *Chem. Zeit.*, 1909, 33, 949; *J. Soc. Chem. Ind.*, 1909, 28, 1030.

⁶ According to Schindler (*Chem. Zeit.*, 1908, 32, 314; *J. Soc. Chem. Ind.*, 1908, 27, 497), cotton contains approximately 0.25 per cent. of nitrogen. This amount is, however, greatly reduced in the various processes through which the cotton has to pass, and it can, therefore, be neglected.

manner, and is then ready for the nitrogen estimation. The result is calculated as follows. If, for example,

0.4853 g. of material were found to contain 8.88 per cent. N.

Since wool contains 14 per cent. N.:—

$$14 : 100 = 8.88 : x$$

$$x = \frac{100 \times 8.88}{14} = 63.43 \text{ per cent. wool.}$$

It is not necessary to remove any finishing material present by treatment with hydrochloric acid; the removal of fats, etc., is, however, essential. A. Pinagel¹ considers this method useless since the sample used for the Kjeldahl estimation is of necessity too small, and can, therefore, not be considered as an average sample. He considers the method of dissolving the wool in sodium hydroxide solution best suited for the purpose. The removal of finishing materials is first effected by means of diastase. A piece weighing about 100 g. should be used for the examination. It is, however, necessary to employ a proper conditioning stove.

2. *Silk, Wool, and Cotton*.—Rémont's method,² can be employed for the estimation of the four most important textile fibres, but cannot be used for heavily weighted black silks.

Four samples of 2 g. each are taken. Three of these are used for testing, whilst the fourth is put aside.

Estimation of Finish and Dyestuff.—The samples are immersed in 200 c.c. of a 3 per cent. solution of hydrochloric acid, and boiled for fifteen minutes. If the liquor becomes highly coloured it is decanted, fresh acid is added, and again boiled for fifteen minutes. The samples are then washed, the water pressed out, and dried. The cotton is readily stripped, wool less readily, silk very imperfectly. Light shades dyed with coal-tar dyestuffs can be neglected as regards silk, but in the case of black or dark shades the weight must be taken into account. Aniline black is very rarely used on silk, whilst logwood-iron blacks, by means of which the weight of the fibre can be increased by more than two-thirds of its original weight, is largely used. Logwood-iron black can be removed completely if it does not exceed a quarter of the weight of the silk, but above this quantity it is only partially stripped. This may be verified by incinerating a washed sample.

Separation of Silk.—One of the purified samples is placed apart whilst the other two are immersed in a boiling solution of basic zinc chloride of sp. gr. 1.600. This reagent is prepared by mixing 1000 parts of fused zinc chloride, 850 parts of distilled water, and 40 parts

¹ *Elsäss. Textilblatt*, 1910, p. 90; *Chem. Zeit. Rep.*, 1910, 34, 455.

² *Chem. Zeit.*, 1881, 5, 972; *J. Soc. Chem. Ind.*, 1882, 1, 64.

of zinc oxide, and heating until dissolved. The two samples are then washed until ammonium sulphide ceases to give a precipitate with the washings. The washing may be accelerated by pressing the samples between a piece of linen cloth.

Separation of Wool.—One of the two samples which have been freed from silk is put aside, and the other is boiled gently for fifteen minutes with 60-80 c.c. of sodium hydroxide solution (1.5 per cent.), then carefully washed, as above, in order to avoid any loss of material.

Drying and Weighing.—The four samples are dried at 100° for one hour, then placed in the air until the following day, and weighed. The part which has not been treated should weigh 2 g. The difference in weight between this and the one treated with acid alone, gives the amount of finishing material and dyestuff present. If the weight of the piece treated with zinc chloride is subtracted from the weight of the second piece, the weight of silk present in the fabric is obtained. The fourth piece consists of vegetable fibres, to the weight of which must be added 5 per cent. (fibre destroyed during boiling with sodium hydroxide). The weights of the different fibres multiplied by 50 give the percentages, and the difference between the sum of these and the total 100 gives the percentage of wool present in the sample.

D.—The Examination of Weighted Silk.

Since the so-called tin-phosphate-silicate process of weighting silk has become generally used, both the qualitative and quantitative analysis of the different kinds of weighting materials has greatly increased in importance. The following weighting materials are used:—

For Colours: tin, phosphoric acid, silicic acid, alumina, zinc, lead, antimony, tannic acid, glue, tungstic acid, sugar, starch, dextrin, glucose, glycerin, gum, oil, and water. Oil, dextrin, glycerin, etc., are not to be considered as loading materials in the proper sense of the word, but as a rule are added in order to improve the feel of the material.

For Blacks: tin, phosphoric acid, silicic acid, iron oxide, chromium oxide, ferrocyanic acid, lead, alumina, zinc, tungstic acid, sugar, glucose, glycerin, oil, gum, tannins, water, etc.

Qualitative Examination.

O. Steiger and H. Grünberg¹ have described the following method of examination:—

Oils and fatty acids:—The fatty acids are usually derived from the decomposition of soaps and oils, or they may have been added in

¹ *Qualitativer und quantitativer Nachweis der Seidenchargen*, Zürich, 1897. See also, *Koloristische und textilchemische Untersuchungen*, P. Heermann, 1903, p. 200.

the finishing of the silk. Unsaponified oils are generally used in the process of "Scrooping." They are extracted either by ether or petroleum spirit. On evaporating, the fats and oils, etc., remain as a residue. Quantitative results may be obtained by this method.

Sugar, dextrin, glycerol, gum, and possibly also lead, glue, and starch, are removed by cold water. Sugar, after inversion, is detected by means of Fehling's solution; dextrin and starch with iodine solution; glycerol by the acrolein reaction; lead with sulphuretted hydrogen, etc.

Glue and tannins if not fixed with iron, tin, Prussian blue, etc., and lead and tungstic acid, dissolve in water at 50°-60°. Ferric chloride gives either a dark green coloration or a dark green precipitate with a solution of tannic acid. In the presence of dyestuffs or other substances which are precipitated by tannic acid, the reaction is not reliable. It is then necessary to remove the dyestuffs before applying the test. According to Steiger and Grünberg, the presence of tannin excludes that of tungstate and lead, but not necessarily that of glue.

Tannins, glue, and ferrocyanides as well as small quantities of antimony, tin, and tungstic acid are removed by treatment with a 2 per cent. sodium hydroxide solution at 30°-40°. On acidifying and adding a ferric salt, Prussian blue is re-formed. Dilute hydrochloric acid (5 per cent.) at 50°-60° partially dissolves tin, alumina, iron (if not present as Prussian blue), tannic acid, and phosphoric acid. The resulting solution can then be tested for ferrous salts with potassium ferricyanide, and for ferric salts with potassium ferrocyanide. The silk treated in this manner may still contain catechu (if dyed brown), tin, alumina, phosphoric acid, and silicic acid. The four last-named constituents are found in the ash of the sample.

Tin:—The method recommended by J. Peroz¹ is to incinerate the fibres and to examine the residue by means of the blowpipe reactions; or to heat the silk in a test tube with an adequate quantity of concentrated hydrochloric acid for a few moments, or until completely dissolved, dilute with water, filter, and test the filtrate with sulphuretted hydrogen.

G. Gianoli and Zappa² recommend mercuric oxide in order to decompose the Prussian blue. The other constituents are then extracted by treating with a solution of potassium binoxalate (5 per cent. at 50°-60°), sodium carbonate solution (2 per cent. at 60°), and then alternately with solutions containing 3 per cent. of sodium sulphide and 2 per cent. of hydrochloric acid.³

¹ *Monit. Scient.*, 1887, p. 597; *J. Soc. Chem. Ind.*, 1887, 6, 565.

² *Chem. Zeit.*, 1900, 24, 620; *J. Soc. Chem. Ind.*, 1900, 19, 897.

³ Cf. also, Heermann, *Färber-Zeit.*, 1909, 20, 75; *J. Soc. Chem. Ind.*, 1909, 28, 361.

*Quantitative Examination.*¹

According to Persoz, the silk is placed for a few moments in concentrated hydrochloric acid to which 2 or 3 vols. of water have been added, then exposed to the air, and dried at 120°. The silk is thus readily converted into a fine powder, in which the amount of nitrogen is estimated. Pure silk fibre contains about 17.5 per cent. of nitrogen. Steiger and Grünberg, as a result of a considerable number of estimations, take the nitrogen-content as 18.33 per cent.; 1 part nitrogen corresponds to 5.455 parts fibroin.

E. Königs first ascertains the amount of water in the silk, then the amount of fat by extracting with ether, and then removes the gum-like covering of the silk by boiling with water. From the residue the Prussian blue is removed by treatment with alkali. This is then estimated by re-precipitating with acid, filtering, and igniting the precipitate with the repeated addition of nitric acid. 1 part of the ferric oxide formed is equivalent to 1.5 parts of Prussian blue.

The oxide of tin present is also estimated and calculated as the compound with catechu tannic acid. 1 part of oxide of tin is equivalent to 3.3 parts of this compound. Finally, the total iron oxide is estimated. If from this the amount of iron oxide found to be present in the form of Prussian blue, and that which is present in the natural silk (0.4 per cent., in raw silk 0.7 per cent.) is subtracted, there remains the iron oxide which is present in combination with the tannic acid of either catechu or chestnut extract. 1 part of iron oxide is equivalent to 7.2 parts of tannate of iron. If ferrous compounds of this type are present, the proportion is 1:5.1.

M. Moyret recommends the following method:—

(1) *Estimation of Water.*—Dry 10 g. of silk at 120°–130° until the weight remains constant. If more than 15 per cent. of water is present, it may be assumed that the silk has been weighted with hygroscopic materials.

(2) *Weighting Materials soluble in Water.*—Dry the silk, boil in distilled water, wash, dry, and weigh. Glycerol, sugar, magnesium sulphate, etc., are dissolved.

(3) *Petroleum Spirit or Ether Extract.*—Wash the silk, dry, and completely extract with ether or petroleum spirit; evaporate, weigh,

¹ Cf. also, R. Gnehm and W. Dürsteler, "Beitrag zur Untersuchung beschwerter Seide" (*Färber-Zeit.*, 1906, 14, 233, 249, 269, 286, 299; *J. Soc. Chem. Ind.*, 1906, 25, 1069); W. Dürsteler, "Beitrag zur Untersuchung beschwerter Seide" (*Inaug.-Dissertation*: Zürich, 1905); Ristenpart, "Kritische Studien zur Analyse der Seidenerschwerung" (*Färber-Zeit.*, 1907, 18, 273, 294; 1908, 19, 34, 53; *J. Soc. Chem. Ind.*, 1908, 27, 329); Sisley, *Rev. Gén. Mat. Col.*, 1907, 11, 97; *J. Soc. Chem. Ind.*, 1907, 26, 605; G. Gianoli, *Rev. Gén. Mat. Col.*, 1907, 11, 300; G. Gianoli, and G. Colombo, "Bemerkungen zur Analyse der Beschwerter Seiden" (*Chem. Zeit.*, 1907, 13, 241; *J. Soc. Chem. Ind.*, 1907, 26, 252).

and examine the extract. This will show whether inferior oils or soaps have been used, which may cause rancidity of the silk.

(4) *Action of Hydrochloric Acid*.—Treat the sample with dilute hydrochloric acid (1 : 2) for a quarter of an hour at 30°-40°. Iron and tannic acid weighting can be recognised by the reddish-yellow colour of the silk and the dark dirty brown colour of the solution which does not become violet on the addition of lime. If the colour of the solution is reddish, and if it becomes violet on the addition of lime-water, logwood black has been used. If the fibres become dark green, the solution yellow, and if lime-water produces no change of coloration, Prussian blue is present. If the fibres turn green, the solution pink, which changes to violet on the addition of lime-water, logwood black, dyed on a bottom of Prussian blue, has been employed.

Metallic mordants such as iron, chromium, aluminium, can be identified in the solution.

(5) *Action of Alkalis*.—After the above treatment boil the silk with a solution of sodium carbonate; tannins are dissolved, and their presence is verified by adding a solution of an iron salt.

(6) *Estimation of Ash*.—Place a weighed sample of the material in a porcelain crucible, incinerate and ignite. If more than 1 per cent. of residue remains, the silk has been weighted. The ash is then further examined.

(7) *Colouring Matters* may often be identified by treatment of the fibres with hydrochloric acid.

A simple process is recommended by E. Ristenpart¹ when the samples are so small that other methods cannot be employed. Absolute accuracy is not claimed for this method, but it may be useful when it is merely a question of approximately estimating the amount of weighting. The method is essentially based upon the fact that with the increase in weight of the cocoon threads, the size of their cross-sections also increases. At the same time a very slight shortening of the fibre takes place which reaches a maximum of 5 per cent., and can, therefore, be neglected. If the weighted and the unweighted threads are considered to be of equal length, all that is required is to ascertain the weights of equal length units from which the degree of weighting can be readily calculated. The weight of 1 m. of the weighted cocoon thread is obtained as follows:—10 m. of the silk thread are accurately measured and weighed. The weight obtained is then first divided by 10 and then by the number of cocoon threads contained in the thread. They are counted with the aid of a pocket microscope. At least ten threads should be examined, from which the mean is taken.

The average weight in milligrams of a metre of the different kinds

¹ *Färber-Zeit.*, 1907, 18, 297.

of the raw cocoon threads used in practice is given in the following Table :—

Italian Organzine	0.160	Kanton Organzine	0.102
Italian Tram	0.151	Kanton Tram	0.088
Japanese Organzine	0.151	China Organzine	0.111
Japanese Tram	0.147		

The method cannot be employed if it is impossible to ascertain the kind of raw silk used.

"The Nitrogen Method," although somewhat complicated and tedious, is, however, preferably used on account of its general suitability. It depends upon the estimation of the fibroin-content by ascertaining the quantity of nitrogen in the sample.

The proposal to estimate the amount of weighting present in a silk by estimating the nitrogen in the fibroin was first made by Sainte Claire-Deville.¹ Moyret² and Persoz³ devised a practical method for carrying out the estimation. The method was further perfected by Steiger and Grünberg. It consists in estimating the amount of nitrogen in the material; from this is calculated the amount of fibroin, and finally from the fibroin the amount of raw silk present. Since silk may also contain silk glue and other substances containing nitrogen, such as ammonium phosphate, Prussian blue, glue, dyestuffs, etc., it is necessary to remove these before proceeding with the estimation. The method is carried out as follows :⁴—

(a) *Quantitative Estimation of the Weighting Materials in Dyed Silk.*—Treat 1-2 g. of the sample with boiling soap solution (20-30 g. per litre) for two hours. Dyestuffs and (in the case of souple and ecru silk) the sericine are removed. Then treat with boiling sodium carbonate solution (sp. gr. 1.01) and add water from time to time in order to keep the concentration of the solution uniform. Ammonium salts contained in the weighting are removed. Now wash the silk well, and dry, and estimate the nitrogen. This is accomplished by employing a modified Kjeldahl method. The process is considerably simplified if the major portion of the weighting materials is previously removed by first treating with hydrofluoric acid, and then with a sodium carbonate solution.⁵ Place the pure fibroin (it should weigh about 0.5-0.8 g.) in a flask of about 200 c.c. capacity with 30-40 c.c. of concentrated sulphuric acid and some dehydrated copper sulphate, and heat for four to six hours. According to W. Dürsteler,⁶ the usual method, *i.e.*, the use of

¹ *Essai sur le Conditionnement*, 1878, p. 487. ² *Le Textile de Lyon*, 1880, p. 93.

³ *Monit. Scient.*, 1887, p. 597; *J. Soc. Chem. Ind.*, 1887, 6, 565.

⁴ For further details, *cf.* Steiger and Grünberg, *Qualitativer und Quantitativer Nachweis der Seidenchargen*; also, Silbermann, *Chem. Zeit.*, 1896, 20, 472; *J. Soc. Chem. Ind.*, 1896, 15, 563.

⁵ *Cf.* Zell, *Z. Farb.- u. Text.-Chemie*, 1903, 2, 239; *J. Soc. Chem. Ind.*, 1903, 22, 825.

⁶ *Dissertation*: Zürich, 1905, p. 16.

sulphuric-phosphoric acid, with the addition of some mercury, is preferable. The decomposition is finished as soon as the liquid becomes coloured green. Now remove the flask from the flame and add potassium permanganate crystals until the liquid becomes a dark green colour. After cooling, dilute carefully with water, and when quite cool pour the contents into a copper distilling flask. Rinse the flask with water and add an excess of concentrated sodium hydroxide solution. Then heat and pass the ammonia liberated into acid, and titrate the excess of acid with alkali.

1 part of nitrogen corresponds to 5.455 parts of fibroin (taking fibroin to contain 18.33 per cent. of nitrogen).

The amount of weighting in per cent. (p) is, therefore :—

$$p = \frac{f-r}{r} \times 100.$$

f = weight of dyed silk.

r = weight of raw silk.

It should be stated that the weighting in per cent. is calculated on the weight of the conditioned raw silk. The weight of raw silk (r) consists of fibroin, sericine, and 11 per cent. of water, the latter calculated upon the total weight of fibroin and sericine.

Thus, for example, a silk is described as weighted 40 per cent. over "pari" if, during dyeing, 1000 g. of the raw silk is increased to 1400 g.

Accurate results can only be obtained if the loss due to the boiling-off of the raw silk is known. This loss varies considerably. The mean values which have been found in the Conditioning Houses of Paris and Zürich are as follows :—

			Per cent.	Per cent.
Italian silk	.	.	21.5	24.0
Japanese silk	.	.	20.0	...
Chinese silk	.	.	20.0	25.0
Kanton silk	.	.	24.0	...
Chappe silk	.	.	4.0	4.0

For Japanese silk the loss due to boiling-off should, therefore, be taken at about 20 per cent., for yellow Italian silk at 24 per cent.

If the place of origin of the silk is not known, this loss is usually taken at 22.5 per cent. The slight error thus made may be neglected in practice.

P. Sisley¹ proceeds as follows :—A sample 1-2 g. in weight is :

- (1) Boiled in a 25 per cent. solution of acetic acid for ten minutes, in order to destroy the formaldehyde compounds of the silk bast which may be present, then washed in pure water.

¹ *Rev. Gén. Mat. Col.*, 1907, 11, 97; *J. Soc. Chem. Ind.*, 1907, 26, 605.

- (2) The sample is treated with a 3 per cent. solution of sodium phosphate for ten minutes at 50° (this reagent does not attack the fibroin as strongly as caustic alkali), then rinsed in water (this treatment is only necessary for black silk).
- (3) Stripped in a boiling bath containing 3 per cent. of soap and 0.2 per cent. of sodium carbonate, for twenty minutes; this operation is repeated, and the silk finally rinsed in pure water, and dried.

If the method is used for silk which has been tendered, the material is placed in a small bag made of fine cambric, in order to prevent loss. The same precaution should be taken in the Kjeldahl estimation, which is carried out as follows: the stripped silk is heated slowly with 20 c.c. of sulphuric acid, 10 g. of potassium sulphate, and 0.5 g. of dehydrated copper sulphate until frothing ceases. It is then heated to the boil, keeping the flask in a suitable position. The reaction should be completed in from twenty to thirty minutes, when the ammonia may be distilled off. If no data are available as regards the loss due to boiling-off, or the conditioning of the silk before weighting, the loss due to boiling-off should be taken as 25 per cent., and the nitrogen-content of the stripped silk without weighting as 16.36 per cent.

(b) *Quantitative Estimation of Weighting Materials in Black Silk.*¹

1. About 1 g. of dried silk is treated with 100 c.c. of 1 per cent. sulphuric acid at 60° . The solution, which is more or less red in colour, is then filtered. This treatment is repeated until the acid solution is only slightly coloured red. Although two or three extractions generally suffice, as many as four or five are sometimes necessary. O. Steiger² obtained good results by using solutions containing 0.20 to 0.25 per cent. of hydrochloric acid in place of the 1 per cent. solution.

2. The silk is then well washed and digested with 100 c.c. of a 2 per cent. sodium carbonate solution at 80° during one hour. This treatment is repeated until the solution does not give the Prussian blue reaction on the addition of ferric chloride. Two sodium carbonate baths will usually be found adequate.

3. The silk is finally boiled in 100 c.c. of a soap solution (25 g. per litre) for one and a half hours, washed, dried, and the amount of nitrogen estimated as given above under (a).

The number of the different baths should not exceed that which is absolutely necessary, because each filtration, etc., inevitably causes loss of material which appreciably influences the final result. Since it is not always easy to determine the point at which the reaction ceases (and

¹ Cf. Gnehm and Blumer, *Rev. Gén. Mat. Col.*, 1898, 2, 133; *J. Soc. Chem. Ind.*, 1898, 17, 495.

² *Chem. Zeit.*, 1909, 31, 329.

those who do not regularly carry out such analyses will often find this to be the case), several estimations should be made simultaneously.

The method may also be applied to silks, in the weighting of which phenylhydrazine has been used.¹

Stripping Methods.

(a) *Hydrofluoric Acid Method*.—A new process for estimating the amount of weighting material in silk charged with tin-phosphate-silica consists in treating it with hydrofluoric acid. The observation that this acid is capable of removing the mineral matter from the fibres was made simultaneously by A. Müller² and H. Zell,³ by O. Meister,⁴ C. Ris,⁵ and others.

According to Zell, 1-2 g. of silk are treated with:—

- (1) Water at 80°-100° for five minutes.
- (2) 1.5 per cent. hydrofluoric acid in a copper vessel at 50°-60° for fifteen to twenty minutes. The silk is then wrung and pressed between filter paper as completely as possible.
- (3) Half an hour in 5 per cent. hydrochloric acid at 50°-60°, and then rinsed in hot water.
- (4) Boiled for one hour in a 2.5-3 per cent. soap solution in order to remove any sericine present ("souple" or "ecru" silk). The soap is removed by boiling in a hot solution of sodium carbonate of sp. gr. 1.007; the sample is finally well rinsed in hot distilled water, dried, and weighed. The remaining silk then consists of pure fibroin.

Zell employs this method in order to determine whether a sample of silk represents "ecru," half boiled-off or completely boiled-off silk, *i.e.* the proportions of sericine to raw silk or to fibroin. For this purpose, the silk, after treatment with hydrochloric acid, is rinsed in water, dried at 105°, and weighed. It is then treated in the usual manner with soap and sodium carbonate, washed, dried, and weighed. The difference represents the sericine.

Example.—2.3804 g. of weighted China trame, treated with hydrofluoric and hydrochloric acid, washed, dried, and weighed = 1.1686 g. After further treatment with soap, sodium carbonate, and water, drying and weighing = 0.9684 g. = fibroin. Consequently the difference = 0.2002 g. = sericine = 17.13 per cent.

According to Gnehm,⁶ 1-2 g. of the silk, in which the amount of

¹ Dürsteler, *loc. cit.*

² *Z. Farb.- u. Text.-Chemie*, 1903, 2, 160; *J. Soc. Chem. Ind.*, 1903, 22, 622.

³ *Z. Farb.- u. Text.-Chemie*, 1903, 2, 239; *J. Soc. Chem. Ind.*, 1903, 22, 825.

⁴ Cf. R. Gnehm, *Z. Farb.- u. Text.-Chemie*, 1903, 2, 209; *J. Soc. Chem. Ind.*, 1903, 22, 968.

⁵ *Z. Farb.- u. Text.-Chemie*, 1903, 2, 261; *J. Soc. Chem. Ind.*, 1903, 23, 928.

⁶ *Z. Farb.- u. Text.-Chemie*, 1903, 2, 210; *J. Soc. Chem. Ind.*, 1903, 22, 968.

moisture is known, are treated with 100 c.c. of a 2 per cent. aqueous solution of hydrofluoric acid in a platinum dish, turned several times, allowed to stand for an hour at the ordinary temperature, the solution decanted, 100 c.c. of acid of the same concentration added, and allowed to remain in contact with the silk for one hour as before. The acid is then poured off, the silk washed seven times with about 150 c.c. of distilled water during a quarter to half an hour, dried in a well-stoppered weighing-bottle, and weighed until the weight remains constant at 95°-105°. The difference between the weight of the dry silk and that of the treated silk represents the amount of weighting material present. By means of a simple calculation the "percentage above pari" may be readily obtained.

Example.—Weight of sample = 1.0302 g. (loss due to boiling-off, 22 per cent.); wet out in cold distilled water, place into a platinum dish with 100 c.c. of a 2 per cent. solution of hydrofluoric acid, and turn frequently. After one hour decant the solution, add 100 c.c. of fresh acid, pour off after one hour, wash as stated above, press between filter paper and dry at 100°-105°, and weigh. Weight = 0.4176 g.

Silk = 1.0302 g., containing 10 per cent. of water; dry silk = 0.9272 g.; dry silk after extraction = 0.4176 g.; difference (weighting) = 0.5096 g.

The weighting above "pari" is calculated as follows, taking the loss due to boiling-off as 22 per cent. :—

$$0.4176 : 0.5096 = 78 : x$$

$$x = 95.19$$

The dried silk, therefore, consists of :—

$$\begin{array}{l} 78.0 \text{ parts silk} = 100 \text{ parts raw silk (dry).} \\ 95.19 \text{ parts weighting.} \end{array}$$

Total 173.19 parts.

The silk is, therefore, weighted 73.19 per cent. above "pari."

Amount given by the dyer = 75 per cent.

Found by means of the nitrogen estimation = 77.3 per cent.

Dyed silk, according to E. Ristenpart,¹ is treated as follows:—Place the wetted-out sample in a copper vessel in a 10 per cent. solution of hydrofluoric acid for about one hour, and stir twice with a copper rod; wash ten times with water, treat with cold potassium hydroxide solution of sp. gr. 1.052 for five minutes, wash five times with distilled water, acidify with dilute acetic acid, wash five times and dry at the ordinary temperature, and weigh.

According to O. Meister,² the silica can be simultaneously estimated if the hydrofluoric acid extract is evaporated with potassium chloride. The potassium fluosilicate (K_2SiF_6), is washed with alcohol and

¹ *Färber-Zeit.*, 1907, 18, 297.

² *Z. Farb.- u. Text.-Chemie*, 1903, p. 209.

weighed, or, according to Stolba, titrated with normal alkali. The remaining constituents of the weighting, such as tin, phosphoric acid, aluminium, zinc, etc., are present in the filtrate.

(b) *Hydrochloric Acid Method*.—In order to estimate the weighting in silk dyed with a tin-cutch black (without iron, so-called Monopol black), E. Ristenpart¹ suggests the following method:—Place 1 g. of the sample in a 10 per cent. solution of hydrochloric acid for one hour, stir frequently, wash with distilled water, allow to remain in normal potassium hydroxide solution for five minutes, wash thoroughly in distilled water, dry and weigh. In order to obtain accurate results if the weighting contains meta-stannic acid, due to storing of the silk or to the original weighting process, which resists solution,² it is necessary to repeat the two operations. Further proof of the total absence of mineral weighting materials in the silk may be obtained by estimating the nitrogen and by incineration.

P. Heermann³ recommends, especially for the examination of tendered material, to add equal volumes of glycerol and normal potassium hydroxide, to work the material at a higher temperature (about 80°), and to allow the sample to remain in the cooling bath for five to ten minutes.

Ristenpart⁴ does not consider this a suitable modification.

(c) *Oxalic Acid Method*.—Persoz⁵ recommended oxalic acid for removing weighting materials from silk. Tin chloride was at that time usually fixed upon the fibre by means of sodium carbonate, so that all that was necessary was to boil the silk with potassium oxalate or alternately with water acidified with hydrochloric and oxalic acid and with sodium carbonate solution.

For the removal of the tin-phosphate-silicate weighting R. Gnehm and W. Dürsteler⁶ recommend the following method:—About 1 g. of silk is treated with a solution of 3-6 g. of oxalic acid in 100 c.c. of water for half an hour, at 60°-70°. The silk is then pressed and washed three times in hot distilled water. The amount of oxalic acid used depends upon the amount and the composition of the weighting in the silk. If the percentage of weighting is not known, then for the first bath 5 g., and for the second bath 2 g., of oxalic acid should be used. The silk is finally treated twice, each time during twenty minutes, with 100 c.c. of a 2 per cent. sodium hydroxide solution, at 60°-70°, then thoroughly washed and dried.

¹ *Färber-Zeit.*, 1907, 18, 295.

² Cf. *ibid.*, 1908, 19, 34, 53; *J. Soc. Chem. Ind.*, 1908, 27, 329.

³ *Färber-Zeit.*, 1909, 20, 75; *J. Soc. Chem. Ind.*, 1909, 28, 361.

⁴ *Färber-Zeit.*, 1909, 20, 126.

⁵ *Monit. Scient.*, 1887, p. 597; *J. Soc. Chem. Ind.*, 1887, 6, 565.

⁶ *Färber-Zeit.*, 1906, 14, 287; *J. Soc. Chem. Ind.*, 1906, 25, 1069; cf. also, A. Müller, *Z. Farb. Text.-Chemie*, 1903, 2, 161.

(d) *Sulphuretted Hydrogen Alkaline Sulphide Method*.—Persoz¹ employs alkaline sulphide in order to dissolve the stannic acid.

According to Gnehm and Dürsteler,² the tin-phosphate-silicate weighting can be estimated quantitatively as follows:—

- (1) About 1 g. of the silk to be examined is placed in an Erlenmeyer flask with 100 c.c. of hot distilled water and 1 c.c. of 10 per cent. hydrochloric acid. During heating to 70°-80° for half an hour, sulphuretted hydrogen is passed into the solution. The liquor is then poured off and the silk pressed, and again treated in the same manner.
- (2) After washing three times in cold distilled water, the silk is treated for five minutes with 100 c.c. of a 4 per cent. alkaline sodium sulphide solution at 40°-50°; the solution is poured off, the silk pressed, and then,
- (3) Treated for a quarter of an hour with a 2 per cent. solution of sodium hydroxide at 60°-70°.
- (4) Finally, the silk is washed five times for a quarter to half an hour in hot distilled water, then dried and weighed.



FIG. 95.

- a. Silk with 160-180 per cent. weighting.
b. Silk with 360-400 per cent. weighting.

If the weighting still contains alumina, the whole treatment must be repeated.

The various inorganic constituents of the weighting can be estimated by incinerating a weighed quantity of the silk, and estimating the quantities by the usual methods.³

In many cases it is possible to ascertain by means of the microscope whether a silk is heavily or lightly weighted (see Fig. 95).

When lightly weighted, the absorption of the colour by the fibre

¹ *Monit. Scient.*, 1887, p. 597; *J. Soc. Chem. Ind.*, 1887, 6, 565.

² *Färber-Zeit.*, 1906, 14, 269; *J. Soc. Chem. Ind.*, 1906, 25, 1069.

³ Cf. Gnehm and Bänziger, *Färber-Zeit.*, 1897, 8, 1; *J. Soc. Chem. Ind.*, 1897, 16, 234.

can still be noticed; but when heavily weighted, the fibre is entirely surrounded by the weighting materials, and very often this layer appears thicker than the fibre itself.

(e) *Estimation of the Boiling-off of Silk*.¹—Raw silk is very often fraudulently weighted with materials such as soap, oil, fats, vaseline, glycerin, gum, gelatin, mineral salts such as borax, phosphates, silicates, etc. In order to detect such adulterations, the fibroin-content of the silk is first estimated. This should also be ascertained in the case of normal raw silk in order to determine the loss due to boiling-off and to form a more reliable opinion as regards the quality of the silk.²

It is much safer to examine the boiled-off silk than that which contains the bast. The examination is best effected by treating an accurately weighed sample with a boiling soap solution in the manner in which it would be treated in the dyehouse. The silk gum and additions, such as have been named above, are removed. The following method is adopted in the Silk Conditioning House in Zürich:—The silk is boiled with 40 litres of lake water or distilled water, to which 625 g. of finest olive oil soap have been added (Marseilles soap). Not more than $2\frac{1}{2}$ kg. of silk should be boiled at a time. The solution is kept constantly but gently boiling. After boiling for twenty-five minutes, the silk being completely covered by the soap solution, it is taken out of the liquor, wrung, and placed in a fresh soap solution, in which it is again boiled for twenty-five minutes. The silk is then washed until the wash-water remains perfectly clear, and is then wrung and dried. The loss due to boiling-off represents the amount of silk gum (and other foreign substances) which 100 parts of absolutely dry silk lose when treated as above with boiling soap.

In order to distinguish real mulberry tree silk from the wild or tussah silk, Persoz boils the material for one minute with a solution of zinc chloride of sp. gr. 1.45, which dissolves the former, whilst the latter is hardly affected.

E.—Analysis of Shoddy, etc.

This includes all kinds of material made from either old or unused woollen waste or woollen fabrics. Waste of silk, cotton, and linen is, however, also frequently used in combination with the above. The principal kinds are:—

- (1) Shoddy, which is spun from long-stapled material which has not been milled, such as old stockings, etc.

¹ Cf. O. Meister, *Ueber die Bestimmung der Décreusage der Seide*, Zürich, 1898.

² Cf. also, P. Heermann, *Z. angew. Chem.*, 1909, 22, 2257.

- (2) Mungo. Short-stapled, and therefore less valuable than shoddy; made from milled fabrics. In spinning this is, as a rule, mixed with long-stapled materials such as wool or cotton.
- (3) Extract or alpaca. Obtained by carbonising union rags.

Shoddy is more strongly attacked, and therefore swells more quickly than pure wool when treated with alkaline lyes.¹

Quantitative Analysis.—Boil the shoddy in concentrated sodium hydroxide solution; silk and wool dissolve, cotton and linen remain undissolved. Wash, dry, and weigh the residue. In order to estimate the amount of wool in the presence of silk, treat with concentrated sulphuric acid. Silk dissolves fairly rapidly, whilst the wool remains. Wash, filter through a cloth filter, dry, and weigh.

If a complete analysis is required, the amount of water and fat present must be estimated. The water is estimated by drying a weighed sample at 100°. The dried sample is then extracted with petroleum spirit, the solvent carefully evaporated and the residual fat weighed.

Qualitative Examination.—The sample is boiled with a solution of logwood. Wool is dyed, whilst cotton and silk are hardly tinted. Cotton and silk are then distinguished by means of the microscope.

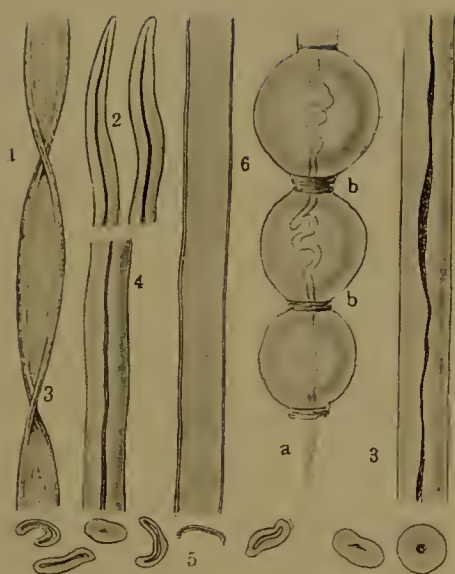
The microscope may also be used for a quantitative examination of the fibres. A number of slides are carefully prepared, care being taken that the individual fibres are placed fairly parallel. By magnifying 20-25 times, and counting the different fibres, the percentage of each kind can be fairly accurately estimated.

Under the microscope most of the wool threads in shoddy consist of differently coloured fibres. The diameter of shoddy fibres is not as uniform as that of the new wool fibre. The fibres frequently narrow down gradually or very abruptly; they then swell strongly, after which they again become narrow. In many cases the wool loses its characteristic scales, whilst in others the fibres are teased so that in places the diameter of the fibre may be considerably less than normal (0.01 mm. and even less). The length of the wool fibres is also of value in distinguishing shoddy; the ends of the fibres are usually split into fibrillæ.

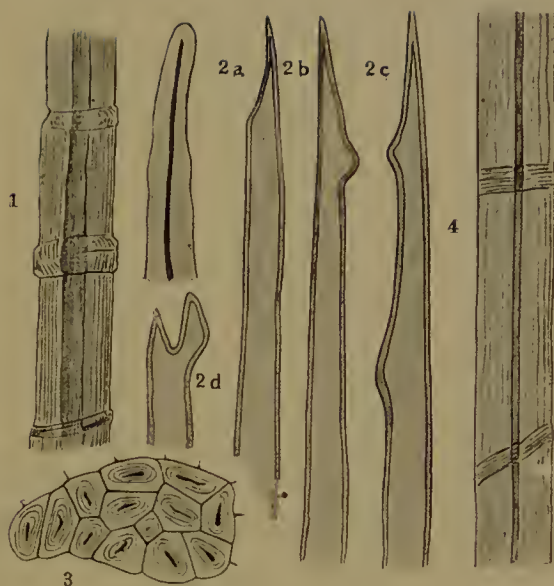
According to L. Pinagel,² there is no absolutely reliable method by means of which the presence of small quantities of shoddy can be ascertained.

¹ According to Hühnel (*Mikroskopie der technisch verwendeten Faserstoffe*), the difference is, however, not distinct.

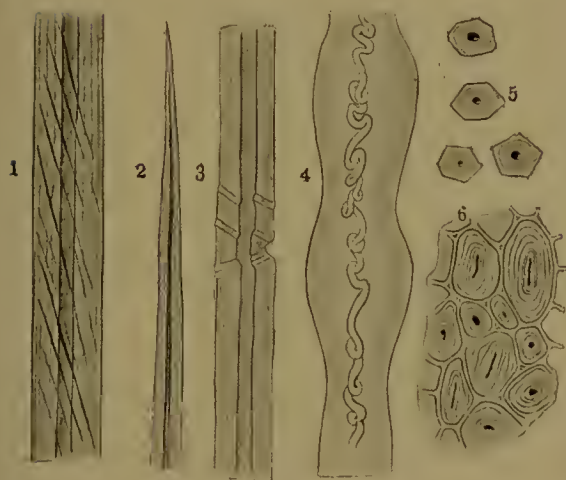
² *Monatsschrift f. Text.-Ind.*, 1910, 25, 125.



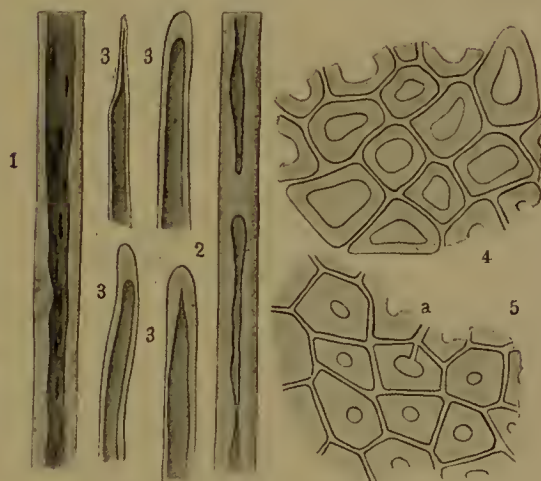
Cotton—*Gossypium herbaceum*, L.



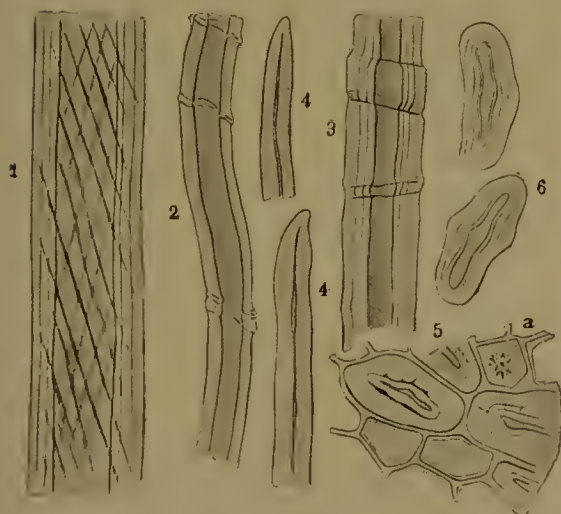
Hemp—*Cannabis sativa*, L.



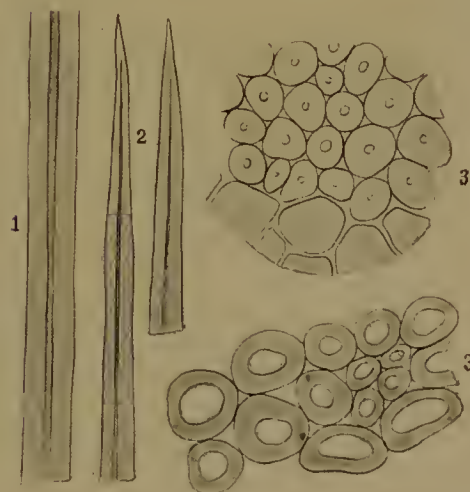
Flax—*Linum usitatissimum*, L.



Jute—*Corchorus capsularis*, L.



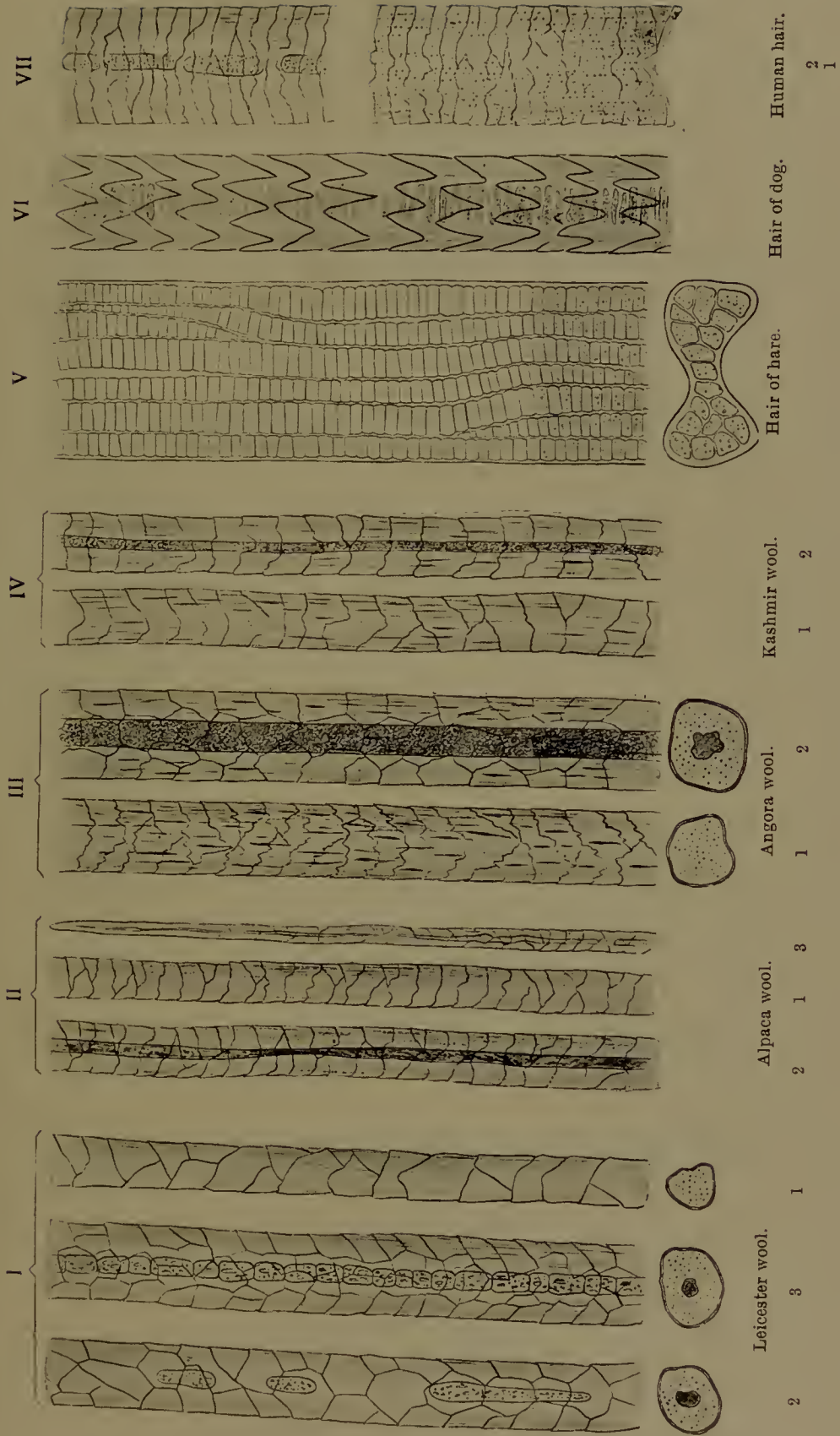
Ramie—*Boehmeria nivea*, Gaud.



New Zealand Flax—*Phormium tenax*, Fors.

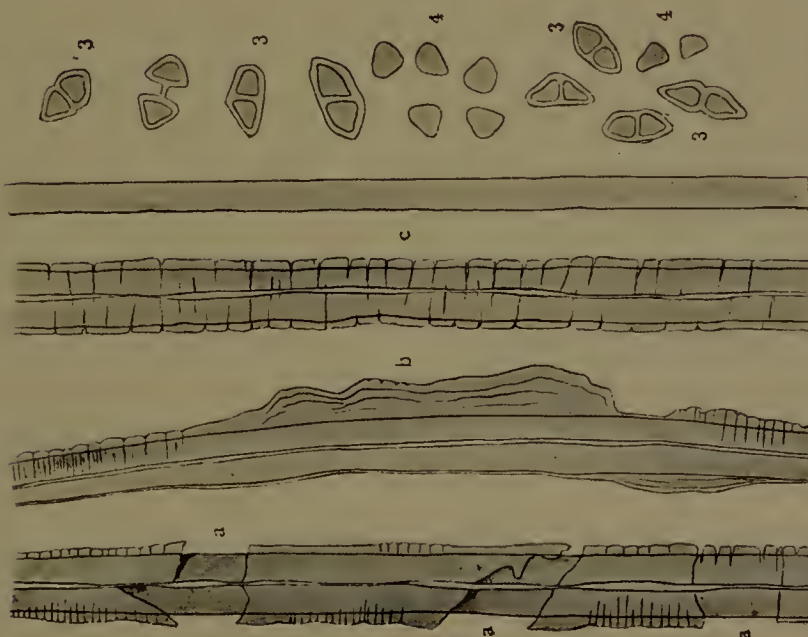
For Explanation of the Plates, see pp. 893-94.

[Between pp. 890-91.]





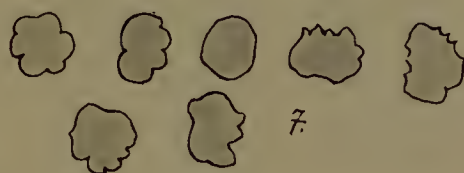
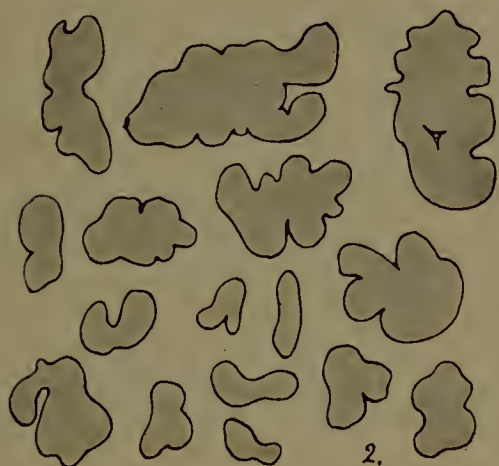
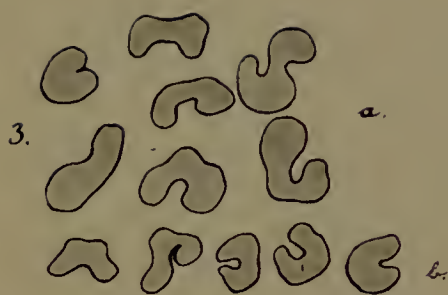
Tussah silk—*Antheraea mylitta*.



Silk—*Bombyx mori*.

1

2



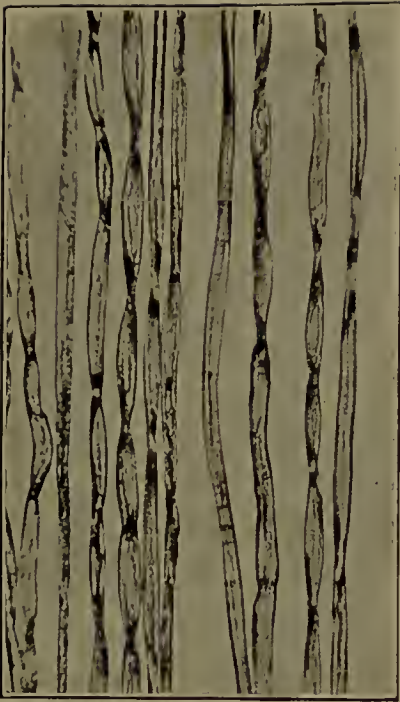


FIG. 1.—Cotton ($\times 100$ diam.).

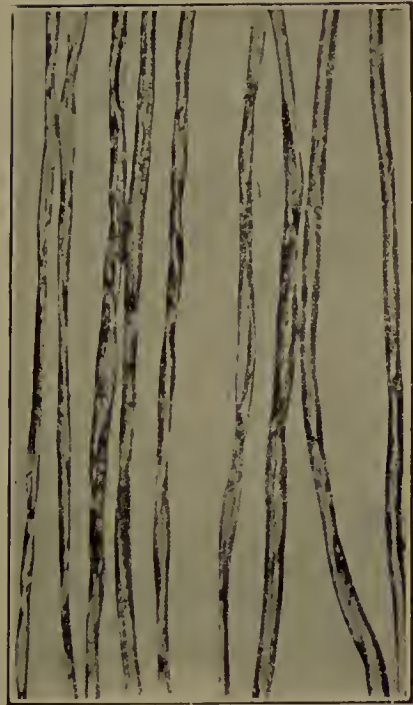


FIG. 2.—Cotton, mercerised under tension ($\times 100$ diam.).



FIG. 3.—Bleached linen ($\times 100$ diam.).



FIG. 4.—China grass ($\times 100$ diam.).



FIG. 5.—Chardonnet silk ($\times 100$ diam.).



FIG. 6.—Pauly silk (*Glanzstoff*) ($\times 100$ diam.).



FIG. 7.—Thiele silk ($\times 100$ diam.).



FIG. 8.—Viscose silk (Coutauld silk) ($\times 100$ diam.).

F.—The Degree of Bleaching of Cellulose.

G. Schwalbe¹ estimates the degree of bleaching of cellulose by its power of reducing Fehling's solution. Over-bleached cellulose possesses a higher reducing power. 3 g. of cellulose cut into small pieces are mixed with 150 c.c. of boiling water; 50 c.c. of Fehling's copper solution and of alkaline Rochelle salt solution are boiled and added to the cellulose. The whole is then heated to boiling, with continuous stirring, and boiled for a quarter of an hour. After filtering and washing, the residue is warmed with dilute nitric acid and filtered. The amount of copper is then estimated in the filtrate electrolytically. The quantity of metallic copper obtained per 100 g. of dry cellulose is given as the "copper value" of the cellulose.² H. Wrede³ has suggested the use of basic dyestuffs in order to distinguish between different degrees of bleaching.

G.—Tests for Oxycellulose and Hydrocellulose.

G. Witz⁴ states that oxycellulose dyes with methylene blue, and that on boiling cotton containing oxycellulose with Fehling's solution, cuprous oxide is precipitated on the fibre. H. Ditz⁵ proposes to make use of Nessler's reagent, with which oxycellulose quickly gives a grey to black colour in the cold, whilst hydrocellulose gives a colour only slowly. Some forms of hydrocellulose, however, act as quickly as the oxycelluloses. Scholl impregnates the fabric containing reducing cellulose with flavanthrene, then pads with sodium hydroxide solution, and steams. Ermen prefers to pad the fabric with a mixture of sodium hydroxide and finely precipitated flavanthrene. Since the value of this method depends on the fineness of the flavanthrene precipitate, he uses a colloidal solution of flavanthrene prepared by bubbling air through an alkaline solution of reduced flavanthrene containing casein. The blue colour produced is not stable. In order to produce a permanent effect, Harrison employs an alkaline silver solution. If ammonia is used to keep the silver salt in solution, it evaporates when the solution is boiled or steamed on cloth, so that the parts not containing oxycellulose become stained. If sodium hydroxide is added to the ammoniacal solution of silver, this staining action is increased, but the parts containing reducing products are coloured very deeply. For

¹ *Färber-Zeit.*, 1908, 19, 33; *J. Soc. Chem. Ind.*, 1908, 27, 156; 1910, 29, 689; *Z. angew. Chem.*, 1910, 23, 924.

² Cf. also, *Z. angew. Chem.*, 1909, 22, 200.

³ *Chem. Zeit.*, 1909, 33, 970; *J. Soc. Chem. Ind.*, 1909, 28, 811.

⁴ *Bull. Rouen*, 1883, 11, 2210; cf. also, W. Harrison, *J. Soc. Dyers and Col.*, 1912, 28, 361.

⁵ *J. prakt. Chem.*, 1908, 78, 348; *J. Soc. Chem. Ind.*, 1908, 27, 1129.

most purposes it is advantageous to have a solution which will not stain pure cellulose, and for this reason sodium thiosulphate was used to keep the silver in solution. The solution is prepared by adding a silver nitrate solution to a solution of sodium thiosulphate, with vigorous stirring, and then adding sodium hydroxide solution. The quantities used are such that the solution contains 1 per cent. of silver nitrate, 4 per cent. of sodium thiosulphate, and 4 per cent. of sodium hydroxide. The pattern may be boiled in the solution, or padded and steamed.

Use can also be made of the property of oxy- and hydrocelluloses of taking up phenylhydrazine. The fabric is first heated on the water-bath with a 1 per cent. solution of phenylhydrazine in glacial acetic acid, thoroughly washed in dilute acetic acid, and then subjected to the silver test given above. The phenylhydrazine intensifies the test considerably.

An alkaline gold solution may be used in place of the silver solution; it produces a violet colour.

III. THE MICROSCOPIC EXAMINATION OF TEXTILE FIBRES.¹

For distinguishing fibres, the microscope is of the greatest importance. The microscopic appearance of the most important textile fibres is shown on Plates I., II., III.,² IV.,³ and in the photo-micrographs by J. Hübner, Plates V. and VI.⁴

The ultra-microscope of Siedentopf can be employed according to Gaidukov⁵ in the examination of dyed and printed textiles. By means of this instrument it is in many cases possible to judge the quality of different spinning fibres and to suggest reasons for differences in the qualities.

The spectro-photometer of Engelmann enables the detection of the most minute quantities of colouring matters, the qualitative and quantitative examination of the different fibres, the comparison of the colouring matters and the fibres dyed with them. It is further possible to compare the spectra of different fibres side by side and also the intensity of the shades of different fibres taken from the same fabric.

For further particulars the original publications should be consulted.⁶

¹ Cf. B. S. Summers, *J. Soc. Chem. Ind.*, 1899, 18, 989.

² Details given by C. Hartwich, sketched by L. Schröter.

³ Sketched by C. Hartwich.

⁴ *Bleaching and Dyeing of Vegetable Fibrous Materials*, 1912.

⁵ *Z. angew. Chem.*, 1908, 21, 393.

⁶ Cf. also, J. Schneider and G. Kunzl, "Spinnfasern und Färbungen im Ultramikroskop," *Zeitschr. f. Mikrosk.*, 23, p. 393; *Fischer's Jahresber.*, 1907, p. 497.

Explanation of the Plates.

(Magnification = 200 times.)

PLATE I.**Vegetable Fibres.**

- Cotton.** 1. Spirally twisted fibre. 2. Ends of fibres. 3. Thick-walled fibre, cross-sections below. 4. Dead fibre. 5. Cross-section. 6. Fibre treated with cuprammonium; (a) Inner canal, twisted; (b) Cuticle, pushed together.
- Hemp.** 1. Fibre exhibiting characteristic joints. 2. Simple point $2a - d$. Widening and fork-like formation of the points. 3. Section of fibre bundle. 4. Fibre with cross-markings.
- Flax.** 1. Fibre spirally striped. 2. End of fibre. 3. Fibre exhibiting joints. 4. Fibre treated with cuprammonium, the inner canal having become twisted. 5. Cross-sections of single fibres. 6. Fibre bundle, cross-section.
- Jute.** 1. Fibre with irregular canal, showing spots. 2. Fibre with irregular canal entirely closed at one point. 3. Ends of fibres. 4. Group of thin-walled young fibres, cross-section. Group of thick-walled old fibres, cross-section with spot (a).
- Ramie.** 1. Fibre viewed from the wider side, exhibiting layers and spiral markings. 2. Fibre seen from the narrower side, exhibiting joints. 3. Fibre viewed from wider side, exhibiting layers of wall and joints. 4. Ends of fibres. 5. Part of a group of fibres from the outer portion of stem, near (a) oxalate crystals. 6. Cross-section of purified fibres.
- New Zealand Flax.** 1. Fibre. 2. Ends of fibres. 3. Cross-sections of fibre bundles.

PLATE II.**Animal Fibres.**

- Leicester Wool.** 1. Fibre without pith. 2. Fibre with reduced pith. 3. Fibre with completely developed pith, and sections of fibres below.
- Alpaca Wool.** 1. Fibre without pith. Fibre with complete pith. 3. End of fibre with reduced pith.
- Angora Wool.** 1. Fibre without pith. 2. Fibre with complete pith, and cross-sections of fibres below.
- Kashmir Wool.** 1. Fibre without pith. 2. Fibre with pith.
- Hair of Hare.** } Above, seen sideways; below, cross-section.
- Hair of Dog.** }
- Human Hair.** 1. Without pith. 2. With weakly developed pith.

PLATE III.**Silk.**

- Silk of Bombyx mori.** 1. Complete threads consisting of the broad fibroin filaments with the coating of sericine. At (a) the coating of sericine has been partly removed; (b) sericine coating more strongly developed on one side; (c) coating broken in many parts, due to drying. 2. Single fibroin filament. 3. Cross-sections of complete threads as (1). 4. Cross-sections of individual filaments as (2).
- Tussah Silk of Antheraea mylitta.** Single fibroin threads showing single filaments. Cross-sections, showing minute specks due to single filaments.

PLATE IV.

Cross-sections of Artificial Silk Threads.

(Magnification = 200 times. Fig. 5a, 60 times.)

FIGS. 1-5, COLLODION SILK. FIG. 6, GLANZSTOFF. FIGS. 7-8, VISCOSE SILK.

- Fig. 1. Lehner silk, 1892. Very thin and regular.
 Fig. 2. From Kessel-Spreitenbach (Switzerland), 1896. Very uneven in thickness.
 Fig. 3. From Glattbrugg (Switzerland): (a) 1904; (b) 1905. Nearly all bent.
 Fig. 4. Collodion silk from Tubize (Belgium), 1911. Flattened.
 Fig. 5. Imitation horse hair from Glattbrugg (Switzerland), 1904. Filaments pasted together.
 Fig. 6. Glanzstoff (so-called N.S. silk) from Oberbruch, 1911. Smooth and nearly circular.
 Fig. 7. Viscose silk from Alost (Belgium), 1911. Striped, cross-sections serrated.
 Fig. 8. Viscose silk from Emmenbrücke (Switzerland), 1910. Less striped than Fig. 7.

PLATES V. AND VI.

Photo-micrographs of Fibres, by J. Hübner.

The description and magnification are given below each photo-micrograph.

IV. MERCERISED COTTON AND ARTIFICIAL SILK.

Mercerised Cotton.

Cotton which has been impregnated, usually either in the hank or in the piece with concentrated caustic soda lye, either with or without tension, but which has been stretched before or during the removal of the soda by means of washing, is termed mercerised cotton. The material, after this treatment, exhibits a silk-like lustre and feel (scroop), which is permanent.

During the process of mercerising, the original creased or folded ribbon-like cotton fibre becomes converted into a straight rod of nearly circular cross-section, which carries on its surface a series of spiral elevations; at the same time the fibre becomes smooth and the rounded surfaces of the ridges reflect the light, *i.e.* the fibre becomes lustrous.¹

The increase in strength of cotton due to mercerising amounts to from 30-40 per cent.

¹ For further information, cf. A. Fraenkel and P. Friedländer, *Mitt. techn.-Gew. Museums*, Vienna, 1893; Vieweg, *Ber.*, 1907, 40, 3876; Ust and Westhoff, *Chem. Zeit.*, 1909, 33, 197; O. Miller, *Ber.*, 1910, 43, 3430; 1911, 44, 728; C. F. Cross, *Ber.*, 1911, 44, 153; J. Hübner and W. J. Pope, *J. Soc. Chem. Ind.*, 1904, 23, 404.

Friedländer has given the following figures for yarn :—

	Test No.	Tearing strain in g.	Elongation in mm.
Unmercerised yarn . . . {	1	360	20
	2	356	20
	3	360	22
Mercerised with soda lye of sp. gr. 1.32 . . . {	1	530	44
	2	570	40
	3	559	35

R. Lange¹ suggests the following reaction for the characterisation of mercerised cotton :—Place the fibre for three minutes in a solution of zinc chloride iodine and then wash. Unmercerised cotton is rapidly decolorised, mercerised cotton loses the blue coloration much more slowly.

H. David² bases a method upon the following observation :—If mercerised cotton is treated a second time with caustic soda lye, its affinity for dyestuffs is not increased. The pattern, if necessary, is first stripped, stretched on a frame provided with pins, and spotted with caustic soda lye of sp. gr. 1.38, and further with this lye diluted with an equal volume and with three times its volume of water respectively. After washing and souring, the pattern is dyed with a direct dyeing dyestuff, such as Congo red. The spotted parts dye a deeper shade if the cotton has not been mercerised, but the same shade if it has been mercerised.

E. Knecht³ has shown that mercerised cotton dyed with benzopurpurin and then treated with hydrochloric acid turns reddish-violet, whilst non-mercerised cotton turns blue. He also suggests the use of benzopurpurin in order to ascertain the degree of mercerisation.⁴

J. Hübner⁵ has shown that mercerised cotton exhibits a greater affinity for iodine dissolved in an aqueous solution of potassium iodide than non-mercerised cotton. If samples which have been mercerised with soda lyes of different strengths are immersed in a *N*/100 iodine solution, along with non-mercerised cotton, it will at once be noticed that the intensity of the brown coloration varies with the concentration of the soda lye used. If the amount of iodine absorbed is ascertained, it will be found that mercerised cotton absorbs more iodine than non-mercerised cotton, and further that, similar to dyeing with the substantive cotton dyestuffs, cotton mercerised under tension absorbs less

¹ *Färber-Zeit.*, 1903, p. 368.

³ *J. Soc. Dyers and Col.*, 1908, 24, 68.

² *Rev. Gén. Mat. Col.*, 1907, 11, 216.

⁴ Cf. also, A. B. Knaggs, *Chem. Zeit. Rep.*, 1908, 32, 314; *J. Soc. Dyers and Col.*, 1908, 24, 112; O. Miller, *Ber.*, 1909, 43, 3430.

⁵ *J. Soc. Chem. Ind.*, 1908, 27, 105.

dyestuff than cotton which has been allowed to shrink during mercerising.¹

A further distinction will be noticed if the cotton which has been immersed in the iodine solution is washed with water. After a few washings the colour changes to chocolate, which rapidly disappears in the case of non-mercerised cotton, whilst that of the mercerised cotton changes to a bluish-black, which disappears more slowly. If a 2 per cent. solution of potassium iodide is used for washing in place of water, the non-mercerised cotton is slowly discoloured, whilst the mercerised cotton remains brownish-black, *i.e.*, it does not change to blue. The blue coloration of cellulose with potassium iodide observed by Schwalbe² has not been noticed. The blue coloration appears immediately if mercerised cotton which has been washed with a potassium iodide solution is finally treated with water.

The reaction is carried out as follows:—The pattern, after having been freed from starch, is immersed for a few seconds in the following solution, along with a non-mercerised sample: 20 g. of iodine dissolved in 100 c.c. of a saturated solution of potassium iodide in water. The samples are then removed from the solution. After washing a few times with water, the non-mercerised cotton becomes white, whilst the mercerised sample remains a bluish-black, which on repeated washing fades the more slowly the stronger the caustic soda lye which has been used in mercerising.

The degree of mercerisation can be still more distinctly observed if a 2 per cent. potassium iodide solution is used for washing in place of water. A direct relation between the strength of the lye used and the depth of the coloration does not, however, exist; thus, when a lye of sp. gr. 1.35 has been used, decolorisation proceeds more rapidly than with one of sp. gr. 1.25.

If coloured samples are to be examined, it is necessary either to discharge the colour by means of any of the well-known agents, or, in the case of light-coloured patterns, to dye the standard pattern to approximately the same shade with dyestuffs similar to those which have been used in producing the pattern under examination. This also refers to the method described below.

The resistance of the iodine colorations can also be tested by exposing the samples to the atmosphere. The same relations exist as observed in washing. The decolorisation may be accelerated by giving the samples a preliminary rinsing either in water or in a 2 per cent. potassium iodide solution. In the former case decolorisation proceeds much more rapidly than in the latter.

Hübner has further suggested another reliable and simple method

¹ Cf. also, Schaposchnikow and Minajew, *Z. Farb.- u. Text.-Chemie*, 4, p. 81.

² *Ber.*, 1907, 40, 1347, 4523; *J. Soc. Chem. Ind.*, 1907, 26, 1107.

for which two solutions are prepared, one containing 1 g. of iodine and 20 g. of potassium iodide in 100 c.c. of water, and another containing in 300 c.c. of the solution, 280 g. of zinc chloride. Shortly before using the reagent, 10-15 drops of the former solution are added to 100 c.c. of the zinc chloride solution. The patterns are wetted out, pressed between filter paper, and then placed in the reagent. Non-mercerised cotton remains white, whilst mercerised cotton soon assumes a dark blue coloration. The depth of the coloration depends, on the one hand, on the concentration of the zinc chloride and the iodine solution, and also upon the degree of mercerisation. By immersing samples of cotton which have been mercerised with known strengths of caustic soda together with the sample under examination, it is possible to ascertain the degree of mercerisation. The blue coloration is also produced on cotton which has been treated with either sulphuric acid, nitric acid, phosphoric acid, or with saturated solutions of zinc chloride, sodium sulphide, or barium-mercuric iodide; but it does not appear when hydrochloric acid, potassium-mercuric iodide, or potassium iodide has been used.¹

T. F. Hanausek² states that cotton which has been mercerised under proper tension can be readily recognised by means of the microscope. He describes the appearance of the fibre as a fairly straight, round, apparently solid, smooth rod. The canal is either visible throughout the entire length of the fibre, varying in width, and usually very narrow, or it is only clearly visible in short lengths. The width is 20-35 μ .

It should, however, be pointed out that in many cases the microscope affords no reliable means of distinguishing mercerised fibres, especially if such fibres have been taken from fabrics which have been mercerised on an industrial scale, because individual fibres have frequently been only incompletely penetrated by the caustic soda solution, whilst other fibres have not been acted upon at all.

In ammoniacal cupric oxide, the properly mercerised fibre swells uniformly without the characteristic bulb-like widenings of ordinary cotton.

Artificial Silk.

The materials used in the manufacture of artificial silk are:—

- (a) Nitrocellulose (collodion).
- (b) Cellulose ammoniacal cupric oxide.
- (c) Viscose (cellulose xanthogenic acid).
- (d) Cellulose acetate.
- (e) Animal substances (glue, casein).

¹ Cf. also, R. Friemel, *Chem. Zeit.*, 1908, **32**, 66, and J. Hübner, *ibid.*, p. 220.

² *Fischer's Jahresber.*, 1905, p. 404.

Large quantities of the viscose, the ammoniacal cupric oxide, and the nitrocellulose silk are at present manufactured, whilst the acetate silk is still of minor importance.

Chardonnet, Lehner, Besançon, Meteor, or Frankfurt Silk.—The filament is uniform but rather thick. The average diameter is 70-80 μ , and, therefore, about four times that of natural and one and a half to two times that of wild silk.¹

As regards strength, etc., the following figures have been obtained:²—

	Denier.	Strength in g.	Elongation per 1 m., in mm.
Artificial silk {	60	69	155
	65	83	171
Trame	60	214	189

The specific gravity is rather higher than 1.5 and is about 13 per cent. higher than that of natural silk.

Chardonnet silk possesses a high but more metallic gloss than natural silk; it is not as soft, much heavier and much less elastic, and has a drier feel than natural silk, and it does not possess the characteristic "scroop"; the strength is inferior to that of real silk and is greatly reduced when the material is treated with hot liquids.

Its great affinity towards artificial dyestuffs (especially the basic dyestuffs) is as a rule sufficient in order to distinguish it from natural silk. The former also burns like vegetable fibres and its solution in potassium hydroxide becomes yellow, whilst that of natural silk remains colourless.

Artificial silk does not dissolve in an alkaline copper solution containing glycerol.³ This solution is prepared by dissolving 10 g. of copper sulphate in 100 g. of water, adding 5 g. of pure glycerol, and then sufficient potassium hydroxide solution until the precipitate formed disappears.⁴ The reaction is quantitative as a means of separating natural and artificial silk.

Under the microscope the fibres appear thicker and more regular than those of natural silk. Valuable information may also be obtained by a nitrogen determination. Artificial silk contains only minute quantities (usually less than 1 per cent.), whilst natural silk contains about 18.33 per cent. of nitrogen.

¹ Silbermann, *Färber-Zeit.*, 1892-3, p. 315.

² E. Herzog, *Färber-Zeit.*, 1894-5, p. 50; O. Schlesinger, *Papier-Zeit.*, 1895, p. 1578; A. Herzog, *Z. Farb.- u. Text.-Chemie*, 1904, p. 259.

³ Cf. Table on p. 904.

⁴ *Färber-Zeit.*, 1894-5, p. 201.

Viscose Silk.¹—Viscose silk burns more slowly than Glanzstoff; it swells strongly in water.

Acetate Silk.—A. Herzog² gives the following reactions for acetate silk :—

- (1) Water causes no swelling of the fibre.
- (2) The specific gravity is remarkably low (1.251).
- (3) Zinc chloride-iodine and iodine-sulphuric acid produce a yellowish coloration.
- (4) Dissolves in cold glacial acetic acid.
- (5) Is not dissolved by copper oxide ammonia.
- (6) Burns like animal fibres.
- (7) In polarised light (crossed Nicols), grey.
- (8) With Congo red the fibres exhibit dichroism.

Vandura Silk (Gelatin Silk, A. Millar's process).—The fibres possess but little elasticity, and break readily. They appear glassy and become soft on warming; they are flattened when ironed. Its optical characteristics have been described by A. Herzog.³

C. Schwalbe⁴ characterises the different artificial silks as follows :—About 0.2 g. of the sample are warmed in a test tube on the water-bath with an equal quantity (about 2 c.c.) of Fehling's solution for about ten minutes. On filling the test tube with water, Chardonnet silk tends to produce a green coloration, whilst Pauly and viscose silk remain a pure blue. A slight deposit of red copper oxide can be clearly seen on the Chardonnet silk.

For the further characterisation of Pauly and viscose silk, zinc chloride-iodine solution is allowed to act for a few moments on equal quantities of the silks; the excess is poured off, the test tube filled with water, and the washing operation repeated until the water is colourless or only slightly yellow. Pauly silk (Glanzstoff) is only slightly coloured, and loses the brownish colour on repeated washing, whilst viscose silk remains green for a considerable time.

P. Maschner⁵ uses concentrated sulphuric acid for the characterisation of the various artificial silks. Nitro-silks remain at first almost colourless, and only after about forty to sixty minutes can a weak yellowish coloration of the acid be noticed. Copper oxide ammonia silk becomes immediately distinctly yellow or light yellowish-brown; after about forty to sixty minutes, the liquid becomes yellowish-brown.

¹ A. Herzog, *Die Unterscheidung der natürlichen und künstlichen Seiden*, 1910, p. 25. As regards behaviour towards reagents, see also K. Süvern and F. Mach, *Färber-Zeit.*, 1903,

14, 54.

² *Chem. Zeit.*, 1910, 34, 347; *J. Soc. Chem. Ind.*, 1910, 29, 555.

³ *Oesterr. Chem. Zeit.*, 1906 (2), 9, 166.

⁴ *Färber-Zeit.*, 1907, 18, 273; *J. Soc. Chem. Ind.*, 1907, 26, 1044.

⁵ *Färber-Zeit.*, 1910, 21, 352; *J. Soc. Chem. Ind.*, 1910, 29, 1299.

Viscose silk becomes immediately distinctly reddish-brown; the liquid after forty to sixty minutes, reddish-brown. After ten to twenty minutes most of the fibres are dissolved, and after two hours they are completely carbonised. The reaction is only reliable when known standards of artificial silks are available.

In order to carry out the test, equal quantities of the silk (about 0.2 g.) and the standard silk (air dry and if possible of the same denier) are placed in small, dry Erlenmeyer flasks which are placed on white paper. Equal quantities of pure sulphuric acid (10 c.c.) are simultaneously poured on the samples. The flasks are shaken a few times, and the change in colour of both the silks and the liquor observed immediately afterwards and during the next hour. The difference is usually most distinct after about forty to sixty minutes. The reaction can also be used on dyed artificial silks, but the colour must be first stripped with either bleaching powder, permanganate and sulphurous acid, or hydrosulphite solution, and the fibres afterwards washed and dried before immersion in the acid.

The method can also be used for the examination of artificial horse hair and artificial straw (Meteor, Sirius, Pan, Silkopan, etc.).

*V. Clement's Method of Examination.*¹—(a) The sample is placed in a solution of diphenylamine in concentrated sulphuric acid. Collodion silk (even if denitrated) gives the blue nitric acid reaction.

(b) Dye with a basic dyestuff: Collodion silk is dyed heavily; cellulose silk (Glanzstoff) is dyed to a medium shade only, even if excess of dyestuff is present.

(c) With Schiff's reagent (magenta solution decolorised with sulphurous acid) collodion silk is dyed heavy pink, viscose silk somewhat lighter, and Glanzstoff still lighter.

(d) The microscopic appearance of cross-sections of the various silks is different. Collodion and other silks obtained from solutions in volatile solvents appear oblong. The cross-sections of the silks obtained from aqueous solutions are irregular if spun as single fibres, but if spun as fibre bundles with preliminary twisting, they appear polygonal and mostly pentagonal. Viscose silk appears more angular, Glanzstoff more rounded. This is due to the fact that the fibres remain soft during the spinning operation, and that they become pressed against each other.

Fibres spun from gelatin and casein are nearly round.

(e) Acetate silk does not readily wet out in water; it contains fixed acetic acid, the presence of which may be ascertained after saponification of the cellulose esters.

(f) Fibres spun from gelatin or casein are very little resistant to water; they burn like real silk and dissolve in alkali.

¹ *Färber-Zeit.*, 1909, 20, 1; *J. Soc. Chem. Ind.*, 1909, 28, 136.

These reactions are sufficient in order to determine the nature of any artificial silk. It is, however, difficult to distinguish viscose silk from Glanzstoff, the reactions being very similar.

*V. Clement's Method for the Differentiation of Natural and Artificial Silk.*¹—With some practice the different silks can be distinguished by their appearance. Further conclusions may be drawn by applying the following tests:—

(a) The fibre is wetted on the tongue; artificial silk becomes much weaker, whilst the strength of natural silk is not affected.

(b) A sample is burnt; silk and fibres prepared from animal matter smoulder and carbonise; cellulose and cellulose derivatives burn steadily.

(c) A sample is examined under the microscope. Artificial silk is thicker and different in appearance.

Collodion silk may be readily distinguished from gelatin silk by means of iodine solution² (1 part of potassium iodide dissolved in 100 parts of water and excess of iodine added). Real silk is dyed light brown to yellow-brown, collodion silk dark violet to black, and gelatin silk dark violet. If the coloured fibres are placed in water, collodion silk becomes blue and is soon decolorised, whilst the two other silks remain unchanged. After two hours they, however, also become decolorised.

W. Massot³ has also examined the artificial silks microscopically, and A. Herzog⁴ has fully described the microscopical, microchemical, optical, and ultra-microscopical characteristics of the various silks. The photo-micrographs accompanying the Tables given in the latter monograph will be found most useful. The ultra-microscopic examination is especially suitable in order to detect impurities.

A. Herzog had previously shown⁵ that natural silks exhibit but little dichroism, whilst in the case of artificial silks, with the exception of gelatin and acetate silk, it is clearly noticeable. By previously dyeing the fibres for one hour at a medium temperature with dyestuffs such as Congo red, benzo-azurin, and methylene blue, and turning them to and fro above the objective-Nicol of the polarisation microscope, a distinct colour change will be noticed.

Fibre dyed with	Basis colour.	Axis colour.
Congo red . . .	Pale red (almost colourless)	Dark red
Benzo-azurine . . .	Red-violet	Blue-violet
Methylene blue . . .	Light blue	Blue

¹ *Färber-Zeit.*, 1909, 20, 1; *J. Soc. Chem. Ind.*, 1909, 28, 136.

² Private communication from Prof. C. Hartwich to Prof. Gnehm. ³ *Chem. Zeit.*, 1907, 31, 799.

⁴ *Die Unterscheidung der natürlichen und künstlichen Seiden*, 1910.

⁵ *Z. Farb.- u. Text.-Chemie*, 1904, 3, 259; *J. Soc. Chem. Ind.*, 1904, 23, 783.

The "basis colour" appears when the length direction of the fibre is placed at right angles to the plane of the polariser, the "axis colour" when it is parallel.

A tabular statement of the most important reactions of natural and artificial silks is appended (pp. 904-905).

FINISHING MATERIALS.

The most important substances used in finishing are :—

- (1) Starches, such as wheat, potato, rice, and maize, etc.; flour; dextrin and other starch preparations; gum arabic, gum tragacanth, plant mucilages, preparation of lichens (Iceland moss), sea-weed (carragheen moss or agar-agar, etc.); glue, gelatin. These substances make the material hard and stiff.
- (2) To produce softness and gloss: Oils (Turkey-red oil), tallow, stearine, paraffin wax, soap, and various kinds of wax.
- (3) Hygroscopic materials, such as glycerin, ammonium salts, magnesium chloride, zinc salts, etc., which reduce the hard feel produced by the stiffening materials.
- (4) Weighting materials: Kaolin (China clay), calcium, barium, and lead salts, grape sugar.
- (5) For tinting the finishing pastes: Ultramarine, Prussian blue, smalts, ochre, indigo carmin, artificial organic dyestuffs. To produce a metallic sheen: Finely pulverised metals or metallic sulphides.
- (6) As waterproofing materials: Aluminium and magnesium salts, solutions of rubber and the like.
- (7) In order to render material fireproof: Sodium tungstate, sodium stannate, ammonium salts (ammonium phosphate), borax, magnesium salts, aluminium salts, silicates, etc.
- (8) Antiseptics: Salicylic acid, camphor, boric acid, etc.

For woollen goods, glue, albumin, dextrin, starch, sea-weeds, water-glass, etc., are usually employed.

For finishing silk fabrics, the following substances are used :—Gums (tragacanth and gum arabic), shellac, gelatin, etc.

It is usually not difficult to recognise whether a fabric has been finished. The presence of a large quantity of foreign substances gives rise to dusting when the fabric is torn.

The chemical examination is carried out as follows.

Estimation of Moisture.—A weighed sample is dried at 100°, until the weight remains constant. The dried material must be weighed in a stoppered bottle.

Important Reactions of Natural

	Natural silks.		
	Silk.	Wild silk.	Mussel silk.
Swelling in water . Burning	Hardly any effect Coke-like residue ; burns with disagree- able odour	Hardly any effect Coke-like residue ; burns with disagree- able odour	Hardly any effect Coke-like residue ; burns with disagreeable odour
Effect of burning gases on litmus paper	Alkaline	Alkaline	Alkaline
Coloration with iodine and sul- phuric acid (Höh- nel) ¹ and with zinc chloride iodine (Herzberg) ²	Yellow to yellowish- brown	Yellow to yellowish- brown	Natural colour, yellow to yellowish-brown
Cold, concentrated sulphuric acid	Weak yellow Rapidly dissolved	Weak yellow Rapidly dissolved	Rapidly dissolved
Glacial acetic acid .	No action either hot or cold	No action either hot or cold	Slight swelling
Chromic acid (half- saturated) ³	Rapidly dissolved on warming	Hot : dissolves slowly ; fibrillæ very clearly visible	Hot : completely dissolved ; well-defined longitudinal markings
Hot 40 per cent. potassium hydroxide	Dissolves rapidly	After prolonged boil- ing disintegrated and partly dissolved	After prolonged boiling disintegrated and partly dissolved ; well-defined longitudinal markings
Ammoniacal cupric oxide ⁴	Fibroin dissolved, sericine not dissolved ; strongly folded	Fibroin dissolves more slowly ; dis- tinct longitudinal markings ; crushed portions rapidly dis- solved	Swells strongly without dissolving
Ammoniacal nickel oxide ⁵	Cold : rapidly dis- solved, colour light brown, sericine in- soluble	Cold : swells ; hot : strong swelling and partial solution ; solution light brown	Cold and hot : swelling without dissolving ; dis- tinct longitudinal markings
Alkaline copper- glycerol solution ⁶	Cold : fibroin dis- solves, sericine in- soluble, liquid coloured violet	Cold : nearly with- out action ; hot : solution with violet coloration of the liquid ; disintegrated	Cold and hot : swells slightly without dissolving
Diphenylamine and sulphuric acid ⁷	Without action	Without action	Without action

¹ Dissolve sufficient iodine in potassium iodide solution that the solution when 2 or 3 cm. (diluted sulphuric acid as used for testing paper fibres). The fibrous material to be tested is paper ; then add a drop of the iodine solution, allow to react for a short time, remove excess of

² Dissolve (a) 20 g. dry zinc chloride in 10 g. of water, (b) 2.1 g. potassium iodide and 0.1 g. clear liquid, and add a trace of iodine ; the solution must be kept in the dark.

³ Mix potassium bichromate with excess of sulphuric acid ; as soon as the chromic acid has

⁴ Copper turnings are treated with strong ammonia until the resulting blue liquid dissolves

⁵ See p. 866.

⁶ Dissolve 10 g. copper sulphate in 100 c.c. water, add 5 g. concentrated glycerol and

⁷ Diphenylamine is dissolved in pure concentrated sulphuric acid. (A small quantity to be

and Artificial Silks.

Artificial silks.				
Collodion	Glanzstoff.	Viscose.	Acetate.	Gelatin.
Striking Burns rapidly leaving very little ash (about 0·1 per cent.) Acid	Striking Burns quickly and leaves practically no residue Acid	Striking Burns more slowly Acid	Not affected Coke-like residue; burns with dis- agreeable odour Acid	Very striking Coke-like residue; burns with smell like burning feathers Alkaline
Blue with reddish- violet tinge, strong reddish-violet swelling	Blue with violet tinge, strong reddish-violet swelling	Blue with violet tinge, strong reddish-violet swelling	Yellow	Yellowish-brown
... Rapidly dissolved ;	... Slowly dissolved ; longitudinal lines at first plainly visible	... Rapidly dissolved, longitudinal lines not present	... Slowly dissolved	Brown Strong swelling without dissolving
No action either hot or cold	No action either hot or cold	No action either hot or cold	Dissolves rapidly in the cold	Cold : splitting crossways ; hot : after prolonged boiling almost completely dis- solved Hot : rapidly dissolved
Cold : slowly dis- solved ; hot : quickly dissolved Swells strongly without dis- solving	Cold : slowly dis- solved ; hot : quickly dissolved Swells strongly without dis- solving	Cold : slowly dis- solved ; hot : rapidly dissolved Swells strongly without dis- solving	Cold and hot : swells without dissolving Swells a little but does not dissolve	Rapidly dissolved
Swells and dis- solves slowly	Swells and dis- solves slowly	Swells and dis- solves slowly	Swells but does not dissolve	Rapidly dissolved
Cold and warm : swelling without dissolving	Cold and hot : swelling without dissolving ; longi- tudinal markings very distinct	Cold and warm : swelling without dissolving and without longi- tudinal markings	Cold and warm : slight swelling, without dis- solving	Cold and warm : curls strongly without dis- solving ; coloured brown
No action after prolonged boiling	No action after prolonged boiling	No action after prolonged boiling	No action after prolonged boiling	Hot : dissolves after a short time
Deep blue	No action	No action	No action	No action

in depth appears a clear red. To be used in conjunction with the "paper sulphuric acid" placed upon a microscope slide and the water is removed as much as possible by means of filter iodine by means of filter paper, add the "paper sulphuric acid," and cover with a cover glass. iodine in 5 g. of water ; mix (a) and (b) together, allow the precipitate to settle, decant the

dissolved add an equal volume of water.
cotton rapidly. (Prepare in small quantities only and immediately before using.)

sufficient potassium hydroxide to dissolve the precipitate formed.
prepared before using.)

Estimation of Foreign Substances.—A weighed sample, about 25 sq. cm., is treated with an extract of malt in distilled water; it is then washed, dried, and weighed. The difference in weight represents the weight of foreign matter present. Undissolved insoluble soaps may be still present after this treatment. To remove these the sample is treated with dilute acid, washed, dried, and weighed. To ascertain the nature and the approximate quantity of the substances present, the fabric is boiled for some hours in water, when the thickening materials, soluble salts, and mineral constituents are removed from the fibre. The liquid is filtered, and the residue and filtrate are then subjected to examination.

Examination of the Filtrate.—The filtrate is concentrated on the water-bath. If on the addition of a drop of iodine a blue colour is formed, starch is present. The highly concentrated solution is then mixed with two to three times its volume of alcohol. Certain salts as well as glue, dextrin, and gum are precipitated. Glue is also precipitated from the aqueous solution by a solution of tannic acid.

Gum and dextrin can be easily distinguished by means of the polariscope, gum being lævo-rotatory, dextrin, dextro-rotatory. Aqueous gum solutions are precipitated by lead acetate at the ordinary temperature, whilst both gum and dextrin are precipitated on warming. If no precipitate is formed with lead acetate, but if there is still organic matter in the solution, caragheen moss is probably present.

By warming the concentrated solution with hydrochloric acid on the water-bath, and then testing with Fehling's solution, the presence of sugar can be detected. Part of the solution is evaporated to dryness, and then treated with acid potassium sulphate; the smell of acrolein indicates the presence of glycerin.

Examination of the Residue.—This may contain weighting materials insoluble in water, such as gypsum, barium sulphate, China clay, etc., which are estimated by the usual methods.

Examination for Fat and Resin.—A small sample is boiled with sodium carbonate solution, and filtered. On adding acid to the filtrate, fatty acids are liberated which float on the surface, whilst a precipitate is formed if resin is present. To estimate the fat quantitatively, a weighed sample is extracted in a Soxhlet apparatus, and the weight of the residue, after evaporation of the solvent, ascertained.

L. Pierre¹ recommends the following method for examining finished materials containing fat, soap, glycerin, gelatin, starch, dextrin, glucose, magnesium chloride, magnesium sulphate, zinc chloride, zinc sulphate, kaolin, talcum, calcium carbonate, etc.:—Dry 30 g. of the material in a weighed beaker glass, remove any fat by repeated extraction (stirring) with petroleum spirit, and filter through

¹ *Ann. Chim. anal. appl.*, 1904, 9, 8.

a small filter. The residue is then boiled in 95 per cent. alcohol, and filtered through the same filter. Soap, glucose, glycerol, zinc chloride, go into solution. The alcohol is then evaporated off, and the residue dissolved in water. The soap in the residue is decomposed by adding hydrochloric acid, and the resulting fatty acids are dissolved in ether. The aqueous solution is diluted with water to 250 c.c., and 50 c.c. of this are used for estimating the magnesium as pyrophosphate, and another 50 c.c. for estimating the zinc as sulphide. Glycerol is detected by the syrupy appearance of the evaporated residue, and may be estimated in 100 c.c. of the dilute solution by the method usually employed in the analysis of wine (see p. 766). In the remaining 50 c.c. the glucose is estimated by means of Fehling's solution.

From the residue after extraction with alcohol, dextrin and sulphates may be removed by treatment with cold water, provided the starch is not in the form of a paste. Dextrin is inverted by boiling with dilute hydrochloric acid, and magnesium and zinc are estimated by the usual methods. The starch in the residue is also converted to sugar, and the calcium is estimated as oxalate. Water, silica, and alumina are estimated in a separate sample; the former by drying 5 g. at 110° until the weight remains constant, and the two latter by treatment with fusion mixture. Gelatin is determined by treating the aqueous extract with tannic acid. The amount of gelatin present is found by multiplying the amount of nitrogen estimated by Kjeldahl's method in a 2 g. sample by 6.5. The magnesium chloride is calculated to $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the magnesium sulphate to $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, kaolin to $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, and talcum to $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$.

According to W. Massot,¹ many preparations have lately been introduced, which have found important technical applications, such as nitrocellulose, acetyl-cellulose, viscose, gum tragasol, monopol soap, monopol oil, and diastafor.

Among inorganic substances, which are used for special purposes, should be mentioned:—

Fireproofing materials (in addition to those given above, p. 903):—titanium salts in combination with stannates.

Weighting materials:—Calcium chloride (in place of magnesium chloride) when high temperatures cannot be avoided.

For disinfecting purposes:—Salicylic acid, boric acid, borax, formic acid, formalin, α - and β -naphthol, zinc chloride, sanatol.

The fact that decomposition due to fermentation frequently takes place must not be lost sight of when analysing finishing materials. Thus starch may have been partly or completely converted to dextrin or sugar; a similar reaction may cause plant gums to lose their adhesive properties. Soap is changed owing to the separation of fatty acids.

¹ *Monatsschrift f. Text.-Ind.*, 1906, **21**, 255, 294, 327; 1907, **22**, parts 2-6.

When analysing finished fabrics it is necessary to bear in mind that the quantity of finishing materials absorbed by the fabric is frequently very minute, and, further, that changes similar to those which occur in the finishing pastes may also take place in the finished fabric itself. It is, therefore, in every case necessary to select the method best suited for each particular case.

Part of the sample should be incinerated. The ash should be examined for silicates which may have been used in the shape of China clay, water glass, talcum, etc., then for boric acid and for large quantities of sodium salts. The presence of soluble salts, especially magnesium salts, in the ash is then confirmed by examining the aqueous extract of the ash.

In order to find out in which form the salts have been used, the aqueous solution of the finishing material should be examined for acids, or if this is not practicable, the finishing material should be fused with fusion mixture and potassium nitrate. The fused mass is then dissolved in water, acidified, and tested for chlorides and sulphates.

The microscopical examination of the residue insoluble in water, or of that which remains after extracting finished fabrics, should not be neglected, as this may consist of insoluble loading materials. Tungstates and titanium compounds can be detected by the usual chemical tests.

Although the various constituents of simple mixtures can often be readily detected, in most cases it is advisable to make a systematic examination. A preliminary examination of the aqueous extract, after fatty substances have been carefully removed, will frequently give valuable hints as regards the selection of the method best suited for the particular case. A division of the most important loading materials into two groups can be readily effected by adding 8-10 vols. of concentrated alcohol to one of the concentrated aqueous solution or of the aqueous extract. The detection of the presence of plant gums and similar substances, for which definite reactions are not known, forms the most difficult part of the work.

The thread-like or flocculent precipitate formed when strong alcohol is added and which readily aggregates, but always remains transparent, is characteristic of plant gums and gum tragacanth. In order to carry out the reaction a test tube is filled three-quarters full with either 96 per cent. or absolute alcohol, after which a few cubic centimetres of the concentrated solution to be tested are added. After shaking, the characteristic precipitates mentioned above will be noticed. They will be thread-like in the case of gum tragacanth. Lead acetate produces a lumpy precipitate, which when decomposed on the filter with 50 per cent. acetic acid remains as a thick, shiny mass which cannot be filtered, whilst the smaller particles pass through the filter.

If Fehling's solution is added to part of this filtrate until the precipitate first formed is nearly or completely dissolved, and if then an excess of a 10 per cent. solution of sodium hydroxide is added, a reaction similar to that given by gum arabic under similar conditions will be noticed. The originally clear solution when slightly warmed becomes turbid and shiny flocculent lumps are formed. Precipitates formed by adding lead acetate to solutions of plant gums, if soluble in acetic acid, do not behave in this manner.

To detect gum arabic, 5-6 drops of a 1 per cent. guaiacol solution and 1 drop of hydrogen peroxide solution are added to the aqueous solution of the alcohol precipitate (see above). After shaking, the liquid is allowed to remain in the cold for a time. If gum arabic is present a reddish-yellow, pink, or deep red coloration will be produced.

Glucose solutions used in finishing frequently contain appreciable quantities of diastase. In such cases a white precipitate is obtained on the addition of alcohol, even if no other finishing materials except sugar are present. This white precipitate has the property of converting starch into sugar, which then may be readily detected.

Glucose may also be identified by the phenylhydrazine reaction. After precipitation with alcohol, glucose and glycerol remain in solution. After evaporating the alcohol, a portion of the clear residual liquid is added to a solution of phenylhydrazine hydrochloride and sodium acetate in water. The osazone formation can be readily followed under the microscope, if only the merest trace of sugar is present.

The acrolein reaction for glycerol may be improved upon by using 1.4 nitrophenylhydrazine; the acrolein vapour is allowed to pass over a drop of the hydrazine solution contained in the convex part of a watch-glass. Acrolein causes the formation of orange-coloured flocks which appear as a needle-like, mostly star-shaped formation under the microscope, a conclusive test for even small quantities of glycerol.

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INORGANIC COLOURS

By Prof. A. EIBNER, Ph.D. English translation revised by H. J. L. RAWLINS and A. RULE, D.Sc., Ph.D., Lecturer on Inorganic Chemistry, The University, Liverpool.

THE inorganic or mineral colours comprise naturally occurring substances and artificially prepared products.

Both chemical and physical tests are employed in their examination, which together serve to establish their genuineness and purity, and to determine the properties which are of technical value in their application.

The examination of inorganic colours is considerably complicated by the imperfect and confused character of the nomenclature that still obtains in the industry, both in regard to the pigments themselves and also in respect of the specification of the qualities dealt with. In Germany much attention has been directed to the introduction of a more precise terminology.¹

Apart from the analytical examination of inorganic colours there are many technical properties of importance specifically related to the industries in which they are employed. These include the action of light, moisture and climatic conditions, the colouring and the covering power, the transparency and miscibility, the action of vehicles including oils, water, spirit, etc. These will be referred to in connection with several of the colours dealt with in the sequel. The actual methods employed in the examination of these properties are extremely varied, and are essentially comparative in character; they comprise a number of physical tests, details of which are given in several of the books included in the "Literature" appended to this Section, and such obvious methods of examination and comparison as the specific enquiry under investigation may demand.

I. NATURALLY OCCURRING WHITE AUXILIARY COLOURS; ADULTERANTS AND SUBSTRATA.

The naturally occurring white minerals, with few exceptions, are not employed as body pigments for painting, etc., since as oil colours they do not, in most cases, meet requirements in either purity of tone or

¹ Cf. A. Eibner, *Malmaterialienkunde*, p. 62; also, *Farben-Zeit.*, 1910, 15, 1593; 1911, 16, 597, 819. Details of these proposals are also given in the German Edition, Vol. IV., pp. 449 *et seq.*

covering power. On the other hand, a few such as chalk, gypsum, and infusorial earth are used to a large extent for the preparation of groundwork in fresco painting, in the manufacture of wallpapers and distempers, for lacquer work, in colour printing, also for paper staining and as adulterants. The purest clays such as kaolin (China clay, white bole) are also used, in exceptional cases, as pigments. Powdered heavy spar is, however, employed extensively as a basis or adjunct in the preparation of mineral pigments. Native or, preferably, precipitated barium sulphate, in the form of powder, together with other white substances, serves for the preparation of lake pigments from coal-tar dyes. The detection of these additions and substrata in artificially prepared mineral and organic pigments, and the determination of their purity and applicability, are carried out according to the usual analytical methods. Certain kinds of clay, belonging to the group of acid silicates, have recently been used as colour substrata for combining with basic coal-tar dyes such as malachite green, acid greens, and red and blue basic colours, for the preparation of the lime greens, lime reds, lime blues, etc., used in lime-washing, in the manufacture of wallpaper, etc. (See *Terre verte*, p. 995.)

Calcium Carbonate.

(Chalk; Whiting; English White; Spanish White; Paris White.)

The technically important criteria of chalk are purity of tone and fineness of grain. The removal of accessory constituents is carried out by the levigating process, whereby coloured and argillaceous impurities and the coarser portions are, for the most part, eliminated. The finest kinds of levigated whiting are pure white, and contain only about 1-5 per cent. of impurities insoluble in hydrochloric acid. The degree of fineness of the powder can be determined by means of the sulphurimeter (*cf.* Vol. I., p. 265). The grey-coloured "native chalks" approach the marly limes and marls in composition, with argillaceous constituents up to 25 per cent. The specific gravity of the various chalks is 2.2-2.5. Levigated chalk is used chiefly in distempering, for the preparation of painting grounds, and in the manufacture of wallpapers. It is not used in oil painting, for when mixed with oil it possesses too little covering power, dries very slowly and sometimes incompletely, and its appearance is not pure white. It is employed, however, for making putty. As a diluent for dry colours whiting is seldom used, although nothing disadvantageous is known as regards its compatibility with such colours.

Quicklime.

In estimating the utility of lime for the purposes for which it is employed, viz., as a colour and a binding medium in lime-washing

and fresco painting, little use is made, as a rule, of analytical and physical tests, as it is usually flaked at once and thereby partly purified. Nevertheless the chemical analysis of the raw material is of importance. Its value is determined by the amount of argillaceous constituents, magnesium carbonate (dolomitic lime), silica, iron pyrites, and organic impurities present. The argillaceous constituents have less influence on the quality than the presence of any considerable quantity of magnesium carbonate, as in the slaking process they mostly sink to the bottom. On the other hand, the burnt magnesia mixes with the lime and makes it thin; that is, it then contains comparatively little plastic and dissolved calcium hydroxide, and is rendered granular, "thin," and less binding. Limestones containing a large amount of clay and, especially, of silica, become "dead burnt," owing to the formation of undecomposable or difficultly decomposable calcium and aluminium silicates. Limes of this nature contain a comparatively large amount of so-called "cores" or particles consisting of calcium silicates which only become slaked after a considerable time; these are particularly objectionable when the lime is used for fresco painting, as they may cause subsequent loosening of the layers of material on which the picture is painted. According to A. W. Keim, products of this nature also bring about changes in certain pigments, such as ultramarine, on account of silicate formation.

The slaking of lime certainly removes most of the objectionable matter, but at the same time a careful valuation of the lime as is customary in the manufacture of mortar and cement, is desirable. The chemical methods of estimating the value of lime by means of the calcimeter, and the technical methods of testing its setting properties, slaking capacity, etc., are described in the section on "Calcareous Cements," Vol. I., pp. 669 *et seq.*

The property possessed by slaked lime of combining with casein to form a very hard and weather-resisting compound, "Casein Lime," has recently found fresh application. The latest technical processes of casein painting on walls, and the application of the so-called "cold water colours" are based on this property of lime. These colours are mixtures of dry slaked lime and powdered casein, and when made into a paste with water the formation of casein lime takes place. There is, however, the disadvantage connected with these mixtures that when they are stored the calcium hydroxide is gradually converted into calcium carbonate, and loses its power of combining with the casein.

Gypsum.

(Mineral White; Light Spar; Satin Spar.)

Ground gypsum, or native gypsum containing 2 mol. of water of crystallisation is the only form in which gypsum is used as an adjunct

for cheapening artificially prepared inorganic pigments such as chrome yellows, ultramarines, Bremen blues, copper-arsenic colours, English reds, and also natural mineral colours. Calcined gypsum cannot be used for this purpose, as it separates out. Gypsum is valued almost entirely according to its hue when in the form of powder ; it is seldom submitted to further technical and analytical examination. The methods of examination are described in the section on "Calcareous Cements," Vol. I., pp. 729 *et seq.* The presence of gypsum in pigments is detected by boiling with water and examining the filtrate.

As regards the suitability of gypsum for mixing with other colours, nothing disadvantageous is known. Calcined gypsum is still sometimes used for this purpose ; in such cases the colours thicken when made up with binding materials containing water.

Barytes.

(Heavy Spar ; Permanent White ; Mineral White ; Precipitated Barium Sulphate.)

This pigment is prepared either from native barium sulphate (heavy spar) or from witherite. In the former case the spar is reduced to barium sulphide by igniting it with coal in retort furnaces, the product converted into barium chloride by means of hydrochloric acid, and the solution precipitated either with dilute sulphuric acid or with a solution of sodium sulphate or magnesium sulphate, special precautions being taken in regard to dilution, stirring etc. In the preparation from witherite the mineral is dissolved in hydrochloric acid, the solution made up to a definite concentration, run off from any insoluble matter, and precipitated as above. Permanent white prepared in this way is of a purer white than that obtained from barium sulphide, and is micro-crystalline. Technically, the chief aim in this preparation is the attainment of the greatest possible covering power by obtaining the precipitate in the finest state of division. According to A. Meissener, a permanent white of comparatively good covering power is obtained from barium sulphate which has been precipitated with sulphates and not with sulphuric acid. This product, after being dried, is strongly ignited, then quenched with water, and ground wet, a process similar to that used in the preparation of lithopone, sulphopone, etc. During the ignition alkali salts brought down with the barium sulphate probably give rise to sintering, whereby the density of the product is increased.

Permanent White usually comes into the market in the form of paste containing about 15-20 per cent. of water. Cracks appearing in the paste are a sign that the maximum allowable degree of dehydra-

tion has been exceeded; it must then be kneaded up again with more water, as when too strongly dehydrated it loses in covering power and fineness and mixes badly with water. Ordinary permanent white is in itself only applicable as a water colour and not as an oil colour, for when mixed with linseed oil it forms a lumpy mass. It loses this objectionable property, however, and can be employed as an oil colour, if it is completely dehydrated and then heated rapidly in a muffle to a bright red heat; the glowing mass is then chilled in cold water, and the mud so obtained ground, dried, and powdered.

The quality of permanent white is tested by A. Mierzinski's method¹ as follows:—A solution of 20 g. of glue in 1 litre of water is prepared, and a small quantity of the permanent white to be tested is made up with this glue solution to a consistence similar to that of the oil colour, and spread on strips of paper. After drying, the pigment, if of good quality, should adhere firmly to the paper, and should not be rubbed off by moderate crumpling. If it does not withstand this test, then it has not been prepared with sufficient care—*e.g.*, it has been precipitated in too coarse condition, or in too acid solution, or both. A good quality of permanent white, when tested with glue, forms a fine, white, even coating which adheres with comparative firmness to the paper.

Uses.—Although permanent white is one of the most unalterable pigments, yet it cannot compete as a body colour with other white pigments on account of its comparatively low covering power in oil vehicles. It is occasionally employed together with native heavy spar for adulterating and cheapening deep-coloured pigments, and more frequently for rendering transparent mineral colours such as Paris blue, "warm" chrome oxide green, etc., fit for use as body colours and paints (*cf.* Mineral blue, Permanent greens, Victoria greens). It is employed extensively in the preparation of pigment lakes from coal-tar dyes, or more correctly for the conversion of these pigments into paints and printing colours of relatively high covering power. For this purpose it is either mixed in the form of paste with the precipitated pigments, and the mixture ground, or else it is precipitated simultaneously with the dye. In these cases permanent white must not be looked upon as an adulterant, but as the substratum necessary for the attainment of the optical and other effects required. Its greater covering power compared with that of powdered heavy spar depends on its micro-crystalline structure. As far as investigations have gone up to the present, heavy spar and precipitated barium sulphate appear to belong to the class of white diluting media for coloured pigments which exercise little or no detrimental effect on the permanence of the latter in light and air.

¹ *Die Erd.- Mineral- und Lackfarben*, 1881, p. 375.

White Clays.

(China Clays ; Kaolin ; Pipeclay ; White Bole ; Porcelain Earth.)

The pure white varieties of clay are used only to a small extent for artists' colours, paints, etc. Beyond this they are only employed in exceptional cases for adulterating coloured pigments. The chief use to which they have recently been put is in the manufacture of certain pigment colours from those coal-tar dyes which are capable of forming with these clays compounds permanent in light. Certain varieties of acid clay which occur near the Rhine, in Hesse and in Saxony, are not only innocuous as far as compatibility with the dyes in question is concerned, but they increase the permanence in light of the latter to such an extent, that these become serviceable and for the most part very good pigment colours only in this form of combination. (See *Terre verte* and *Lime greens*.)

The physical and chemical methods of testing clays are described in the section on "Clay," Vol. I., pp. 569 *et seq.*

The clays are of particular importance as substrata in the ochres and umbers for hydrated ferric oxides, ferric oxide, and oxides of manganese.

II. WHITE PIGMENTS.

White Lead.

(Krem's White ; Flake White ; Pearl White.)

The statements found in most text-books concerning the chemical composition and optical properties of white lead refer to the so-called "chamber white lead" as prepared according to the older Dutch and German (Klagenfurt) processes. These qualities have approximately the composition of a basic lead carbonate, $2\text{PbCO}_3 + \text{Pb}(\text{OH})_2$, and contain on an average 1-2½ per cent. of water, 83½-87 per cent. of lead oxide, and 11-13 per cent. of carbon dioxide. On the other hand, those kinds prepared by the French (English) precipitation process are said to consist almost entirely of neutral lead carbonate. The modern idea of "white lead," as Falk has recently pointed out, is therefore incapable, either from the chemical or from the optical point of view, of only one interpretation. As a matter of fact, the covering power of different qualities of white lead varies considerably.

If the composition of chamber white leads is considered in the physical (optical) rather than in the chemical sense, it is correct to look upon the lead hydroxide, since it is amorphous, as being the agent chiefly responsible for the covering power possessed by these products. This agrees with the fact that the French precipitated white leads have less covering power, as they are crystalline.

Salmonys¹ and more recently G. Hauser² have shown, however, that precipitated white lead, that is, approximately neutral lead carbonate, can also be obtained in the amorphous state, and then possesses even better covering power than chamber white lead.³ New views on the composition of white lead have been put forward by L. Falk.⁴

For the preparation of white lead the purest possible soft lead must be employed. A lead which contains about 0.003 per cent. zinc, 0.003 per cent. iron, 0.005 per cent. antimony, 0.0006-0.0008 per cent. silver, and traces of copper, may be considered suitable for the manufacture. Bismuth is an exception, in so far as it is not only non-injurious, but favours the oxidation of the lead, furnishing an excellent product of great whiteness and covering power. American soft lead contains about 0.75 to 1.0 per cent. of bismuth and 0.0002 per cent. of silver. If the lead used in the Dutch process is too hard for the manufacture of white lead, and acetic vapours are only allowed to act on it for the usual length of time, which in this case is too short, red suboxides are formed.

Copper and iron in the lead are detrimental to the manufacture of white lead. These metals are estimated colorimetrically by Neujean's method⁵ as follows:—20 g. of lead (40 g. if very pure, 10 g. if very impure) are dissolved in dilute nitric acid, and the lead precipitated as sulphate by sulphuric acid; the solution is filtered or decanted off, evaporated to a small bulk, and one half treated with potassium thiocyanate and the other half with excess of ammonia; the colorations so obtained are compared with standard colorations preserved in sealed tubes, and containing known amounts of iron and copper respectively. The injurious effect of silver has been examined by Krämer and Bannow,⁶ according to whom it is the cause of the formation of the red coloration referred to above.

Even Dutch white lead sometimes exhibits this peculiar red cast which, as stated, is said to be caused by a compound approximating to lead suboxide, but may be due to the presence of silver, and which, moreover, is a result of faulty preparation (lack of carbon dioxide, insufficiently long action of acetic acid on the lead). This colour does not always disappear completely during the lixiviation process; in general, chamber white lead possesses a more pronounced yellow cast than precipitated white lead, and is therefore frequently corrected with ultramarine.

¹ *Chem. Zeit.*, 1907, 31, 955.

² *Farben-Zeit.*, 1910, 16, 2475.

³ Cf. Gebr. Hezl and A. Wultze, Charlottenburg. A process for the preparation of a white pigment consisting of normal lead carbonate. Ger. Pat. 174024 (1904).

⁴ *Chem. Zeit.*, 1910, 34, 567; *J. Soc. Chem. Ind.*, 1910, 29, 769; cf. also, H. Hof, *Chem. Zeit.*, 1910, 34, 784.

⁵ *Chem. Zentr.*, 1870, p. 642.

⁶ Cf. Vol. II., Part I., "Commercial Lead," p. 233.

For determining the degree of neutralisation in the preparation of neutral lead acetate by the French process, Pfund¹ uses a 1 per cent. solution of mercuric chloride. If a solution of crystallised acetate of lead of any concentration and temperature is treated with about an equal volume of the mercuric chloride solution, the mixture remains quite clear. If, however, a trace of litharge is dissolved in the lead solution or a drop of basic lead acetate added, a considerable white cloud or precipitate is immediately formed on addition of the sublimate solution. If the test be carried out by gradually adding the sublimate solution, drop by drop, to a small portion of the liquid, and shaking, a permanent turbidity is obtained which is formed the more rapidly the further the liquor is from the neutral point. A warm liquor which becomes cloudy on the addition of the first drop is still strongly alkaline; when this takes place at about the sixth drop, the liquor is less alkaline. If the liquor remains clear when half its own volume of the solution has been added, it will not become cloudy on addition of any further quantity—that is, it contains only neutral acetate. The test is most reliable when equal volumes are used and the sublimate solution is run in from a burette. The acetate solution is removed from the vessels by means of a brass cock at some distance from the bottom, and for purposes of testing, about 1 c.c. is filtered directly into a test glass. Since, in the French process, neutral acetate is regenerated simultaneously with the precipitation of the white lead by carbon dioxide, it is only necessary to prepare it once.

Commercial Qualities of Pure White Lead.—Krem's White is a very hard, pure, chamber white lead which is mixed with thin gum, pressed into square clay moulds, and dried. It has a smooth, vitreous fracture and was made originally in Klagenfurt, where the purest white lead is manufactured.

Flake White is a variety of chamber white lead for which there was formerly considerable demand. It is obtained in flaky pieces by beating the lead plates. Its genuineness can therefore be recognised by its form.

Pearl White is white lead which has been tinted with Paris blue, indigo, or possibly with blue coal-tar colours.

Adulterated Qualities of White Lead.—Since technically pure white lead is too expensive for many industrial purposes, it is treated with white "fillers." The substances chiefly employed are heavy spar and blanc fixe (permanent white), also lead sulphate, zinc white, gypsum, China clay, whiting, clay, bone ash, etc. As long as these adulterated qualities are described as such, no objection can be made against them. It must be taken for granted that the comparatively low covering power of these qualities is known.

Two methods are in use for denoting these products: special

¹ *Dingl. polyt. J.*, 1875, 216, 336.

names, or distinguishing appendices (Numbers, Letters) to the name "white lead." Included in this group are the commercial varieties:—*Venetian white*, which contains equal parts of white lead and heavy spar or "blanc fixe"; *Hamburg white*, which consists of 1 part of white lead and 2 parts of heavy spar; and *Dutch white*, which contains 1 part of white lead and 3 parts of heavy spar. According to the second method of designation the technically pure pigment is described as white lead "pure," and the adulterated varieties are denoted by numerals I., II., III., or 1st, 2nd, etc.

The Analysis of White Lead.

1. *Detection and Estimation of Additions.*—A portion of the sample is warmed with dilute nitric acid; the residue may contain sulphates of barium, calcium and lead, and clay, which are separated by the usual methods. The lead is precipitated in the nitric acid solution; in the filtrate zinc, calcium phosphate (bone ash), barium, and calcium are detected in the usual way.

2. *Estimation of Carbon Dioxide.*—The covering power of chamber white lead increases with the quantity of hydroxide, and decreases as the quantity of lead carbonate increases, so that an estimation of carbon dioxide is practically an estimation of the value of the white lead.

Weise found in:—

White lead of best quality, 11.16 per cent. CO_2 .

White lead of second quality (still very good), 11.68 per cent. CO_2 .

White lead of third quality (still quite serviceable), 12.28 per cent. CO_2 .

Drum residue, very poor quality, 14.10 per cent. CO_2 .

Abnormal products of the chambers, quite useless, 16.15 per cent. CO_2 .

For the estimation of carbon dioxide a portion is finely powdered, dried at 100° , and either decomposed by acid in a Schrötter or similar apparatus, or determined by Lunge and Rittener's method (Vol. I., p. 153).

It follows from the remarks made concerning precipitated white lead, that judgment of the covering power of a sample of white lead from the content of carbon dioxide no longer holds good generally.

In addition to the above the determination of the *Loss on Ignition*, which is proportional to the amount of lead carbonate and water, serves for the valuation of chamber white lead. In unmixed qualities it varies between 13 and 16 per cent., and amounts on an average to 14.5 per cent. Hamberger found in three qualities of white lead 21.9, 22.79, and 22.70 per cent. of calcium carbonate respectively.¹

¹ *Pharm. Zeit.*, 43, 806.

3. *Estimation of Lead Acetate*.—Many older qualities of white lead, especially the "caps" and "loaves," contain small quantities of lead acetate, which originates in the manufacture and from incomplete washing, or is purposely added in order to facilitate the moulding of the "caps" and "loaves," in which forms white lead still, though only rarely, comes into the market. This addition is specially injurious when the white lead is used as an artists' colour, for even when only 1.5-2.0 per cent. is present the pigment rapidly becomes yellow in the oil. White lead of this character gives a sediment when boiled with water, which is rendered turbid by sulphuric acid and is coloured brownish-black by ammonium sulphide. The estimation of the amount of acetic acid present in white lead of this nature is carried out by Stahlschmidt's method¹ as follows:—Dilute sulphuric acid is gradually added to 100 g. of white lead in a tubulated retort provided with a funnel the tube of which extends into the liquid; the retort is attached to a well-cooled receiver. After the evolution of carbon dioxide has ceased, the liquid is heated to boiling for some time, and the distillate, into which no sulphuric acid must be allowed to spurt over, estimated acidimetrically.

4. *Estimation of Lead*.—F. H. Storer² estimates the lead by dissolving 2-3 g. of the sample, in a beaker, in 100-150 c.c. of dilute hydrochloric acid at 40°-50° and immediately introducing into the solution a bright strip of pure zinc on which the lead separates out; the solution is decanted through filter paper which contains a small piece of metallic zinc. The residue in the beaker, consisting of metallic lead, is quickly washed with hot water and transferred to a crucible; the lead collected on the filter paper is rinsed into a porcelain dish, and, after removal of the zinc, added to the contents of the crucible. The metal is finally dried in a current of coal gas.

E. Lenoble³ determines hygroscopic water by drying at 100°; carbon dioxide as loss of weight after addition of nitric acid; lead oxide, provided that no other metals are present, by igniting 1 g. of white lead; acetic acid by distilling 1 g. with tartaric acid; water of combination by calculation.

Specimens of French white lead examined by G. Tissandier contained:—

	I.	II.	III.
White lead . . .	85.25	73.17	44.33
Zinc white	2.12	5.30
Blanc fixe . . .	10.12	19.50	40.25
Calcium carbonate . . .	4.63	...	10.12
Clay	5.21	...

¹ Cf. Bolley-Stahlschmidt, *Handbuch der techn. chem. Untersuchungen*, 6th ed., vol. ., p. 356.

² *Chem. News*, 1870, 21, 137.

³ *Ann. Chim. anal.*, 1899, 4, 118; *J. Soc. Chem. Ind.*, 1899, 18, 693.

5. *The Density of White Lead*.—In forming an opinion on the covering power of white lead a determination of the density is important. It is carried out in a pyknometer filled with toluene.¹ Qualities of low specific gravity (great volume) have the best covering power. White lead rich in neutral carbonate, obtained according to the French method by precipitation, is coarsely crystalline, and therefore does not cover so well as the amorphous and more voluminous white lead prepared by the Dutch process. Conclusions as to the covering power of different qualities of white lead may also be drawn from the determination of the degree of fineness in the Chancel sulphurimeter (Vol. I., p. 265).

6. *Fastness to Light*.—This only concerns white lead as an oil colour. As regards the behaviour of white lead itself in the light, nothing unfavourable is known. White lead in oil often gradually turns yellow, not only in the light but also in the dark. It is maintained that zinc white does not exhibit this property. Whether these statements refer to pure white lead and zinc white is not known. On the other hand, as already mentioned, white lead containing lead acetate turns yellow in the light; this may be the explanation of the above observation.

7. *Behaviour in Mixtures*.—White lead which is technically pure, and therefore free from lead acetate, is unaffected in mixtures with most pigments containing sulphur (ultramarines, cinnabar); for exceptions, *cf.* cadmium yellow (p. 939). The presence of lead acetate renders mixtures with ultramarines unstable. Moreover, white lead is unstable when mixed with lime, and is thus not a lime colour; also, it imparts an orange colour to zinc yellow, yellow ultramarine (barium yellow), and to strontium yellow, owing to the formation of basic lead chromate (chrome orange).² For the same reason zinc greens are also discoloured by white lead. So far as is known at present, white lead behaves normally towards other inorganic and organic pigments, that is, it does not accelerate their decomposition by exposure to light even in the palest mixtures.

Uses.—White lead, in spite of its poisonous character and its sensitivity to hydrogen sulphide, is still used to a wide extent as an oil colour by artists, and also by painters for interior and especially for exterior work, as an equal degree of covering power and atmospheric durability is not attained by substitutes. Moreover, seeing that nowadays five-sixths of the total white lead produced comes into the market as an oil colour, the danger of white lead poisoning is considerably diminished.³

¹ E. Lenoble, *loc. cit.*

² A. Eibner, *Techn. Mitt. f. Malerei*, 1907, 23, 151.

³ *Cf.* E. C. C. Baly, *J. Soc. Chem. Ind.*, 1912, 31, 515; also, H. E. Armstrong and C. A. Klein, *ibid.*, 1913, 32, 320.

White Lead Substitutes.

Owing to the poisonous character of white lead and its sensitivity to hydrogen sulphide, referred to above, a number of white lead substitutes have been introduced. Opposed to these defects are the advantages it possesses of great covering power and stability as an oil paint for open-air work. Such substitutes should be free from the disadvantages attached to white lead, and should at the same time possess those properties for which it is valued. The substitutes put forward up to the present completely fulfil only the former of these two conditions. The first substitute for white lead was zinc white, which is non-poisonous and at the same time is not discoloured by hydrogen sulphide. Then followed various lead preparations, such as *Mühlhaus White* (lead sulphate); *Pattinson's White Lead* (basic lead chloride, $\text{PbCl}_2 \cdot 2\text{Pb}(\text{OH})_2$); and *Freeman's non-poisonous White Lead*, a mixture of lead sulphate, zinc white, baryta white, and magnesium carbonate. These pigments are less poisonous than white lead and are not blackened as rapidly or as intensely by hydrogen sulphide. Their covering power is, however, very inferior to that of white lead, on account of their crystalline condition.

Purex is a basic lead sulphate having approximately the composition $2\text{PbSO}_4 \cdot \text{PbO}$. It is said to be a very resistant paint, and to flow very readily on account of the uniformity and spherical character of the particles.

Pattinson's white is recognised by the fact that it dissolves in dilute nitric acid without effervescence and gives a precipitate with silver nitrate. *Antimony white*, used at one period and consisting of antimonious acid, is now seldom found on the market, zinc white having replaced it.

In addition, *Lithopone*, and a very considerable number of compositions the basis of which is chiefly lithopone mixed with white lead or zinc white, also with whiting, gypsum, magnesia and silica, have been introduced. Such of these substances as contain white lead cannot be described as "white lead substitutes." Many of them were given fancy names in order to disguise their composition, e.g., *Oil white*, *Light white*, *Diamond white*, *Edelweiss*, *Snow white*, *Anti-white lead*, *Albanol*, *Blenda*, *Condor*, *Fixopone*, *Nivan*, *Leukarion*, etc.

None of these substances is in the strict sense a substitute for white lead, for although they do not exhibit its defects, yet they do not approach it either in respect of covering power, or as regards stability as an oil paint for open-air work.

Zinc White.¹

(Snow White; Chinese White.)

The introduction of zinc white as a substitute for white lead in artistic and industrial painting was proposed by Courtois of Dijon in 1780, and in 1786 he began to manufacture it on the large scale. In 1854 the firm of Winsor & Newton, London, put on to the market a particularly dense zinc white under the name of *Chinese white*. Since then this name has been used as a quality designation for the purest zinc white, and this applies also to the name "*Snow white*." In 1840 the artist Leclaire tested the properties of zinc white as a pigment and found them suitable, with the result that it was soon afterwards introduced as an artists' colour. The chief grounds for this were its non-poisonous character and its permanence towards hydrogen sulphide. The question whether as regards its covering power and durability as an oil colour it fulfils the requirements of industrial painting as well as white lead, has not even yet been quite settled. As regards its compatibility in mixtures with other pigments no opinions have been advanced up to quite recently.

The individual qualities of zinc white vary in technical purity and tone according to the purity of the ores employed for its preparation; also in density according to the temperature at which the preparation is carried out. The impurities which occur are oxides of cadmium and antimony, arsenic, lead, iron, unburnt zinc, and coal dust. The zinc white used as an artists' colour and as a paint is generally pure white or of a somewhat yellow cast (cadmium oxide). Individual qualities differ less in degree of purity than in density, and are distinguished by a system of *sealing*, zinc white "green seal" being the whitest and most bulky quality; after this come the brands red, blue, yellow, and black seals. This method of designation, therefore, is used with reference to physical differences in the qualities of technically prepared zinc oxide.

Analysis.—Zinc white should dissolve completely in acetic acid without effervescence. The solution on treatment with ammonium sulphide should give a pure white precipitate, and with potassium hydroxide a precipitate of similar appearance completely soluble in excess of the reagent. If the precipitate with ammonium sulphide is grey, either iron or lead is present; if cadmium is present, the precipitate is yellowish. The amount of water present should not exceed 2-3 per cent.; it must be estimated at the lowest possible temperature. Arsenic and antimony are detected by passing hydrogen sulphide into a warm hydrochloric acid solution. It is often stated that zinc oxide absorbs

¹ Cf. *Le Blanc de Zinc et le Lithopone*, A. Souris, 1912.

carbon dioxide from the air and is converted into the basic carbonate; from the quantitative point of view, however, this reaction does not appear to proceed to any considerable extent. If zinc oxide is suspended in water, and carbon dioxide is passed in for one hour, the deposit, after washing, does not effervesce with hydrochloric acid; on the other hand, a very small quantity of dissolved zinc is present in the filtrate. By passing a current of carbon dioxide over red hot zinc oxide and maintaining it until the latter is cold, no zinc carbonate is obtained. Thus no great significance attaches to the statements that zinc oxide on standing in the air becomes crystalline owing to absorption of carbon dioxide, and thereby exhibits diminished covering power.¹

Fastness to Light.—The fact that zinc oxide becomes darker in the light was discovered by H. F. Link.² According to T. L. Phipson,³ many qualities of zinc white are sensitive to light. He ascribed this phenomenon to the presence of a new element, "Actinium," whose sulphur compound was said to become dark coloured in sunlight owing to reduction, and light again in the dark owing to oxidation. Both J. Cowley⁴ and J. B. Orr⁵ confirmed these statements as regards the sensitiveness to light of certain zinc compounds. Mitscherlich⁶ showed that crystals of zinc selenate change their crystalline form on exposure to light. These statements appear, however, to have been forgotten. It was the discovery of the sensitiveness of lithopone to light that again directed attention to this property of zinc compounds. It is, accordingly, necessary to test the commercial qualities of zinc white in this respect. In these cases, however, the amount of darkening does not appear to be very great.

Another and hitherto little-known property of zinc white appears to be of much greater importance, viz., its *Incompatibility in Mixtures with other Pigments*. On this subject there are only isolated statements, such as those of Russell and Abney,⁷ according to which an addition of Chinese white in colour washes spread on test papers and heated in sealed tubes brought about distinct changes in the colours. A. Eibner⁸ ascertained that zinc white had considerable action on most inorganic pigments in the light, and brought about surprisingly rapid changes in all organic pigments. These phenomena are

¹ Cf. "Die Surrogate in der Lack-, Firnis- und Farbenfabrikation"; also, P. Beck, "Über weisse Bleifarben und die sog. Bleiweissersatzmittel," *Chem. Ind.*, 1907, 30, 270.

² *Über die Natur des Lichtes*, Petersburg, 1808; cf. *Geschichte der Photographie*, by Eder, p. 109.

³ *Chem. News*, 1881, 43, 283, and 1881, 44, 73.

⁴ *Ibid.*, 1881, 44, 51 and 167.

⁵ *Ibid.*, 1881, 44, 12.

⁶ *Pogg. Ann.*, 6, 19, and 12, 144 (from *Photochemie*, by Eder, pp. 153 and 124).

⁷ Cf. A. H. Church, *The Chemistry of Paints and Painting*, p. 340.

⁸ *Farben-Zeit.*, 1911, 16, 1754.

particularly marked when gum arabic is used as a vehicle. Under these conditions zinc white causes alteration in the following inorganic pigments: the chrome yellows, chrome oranges, chrome reds, chrome greens, zinc yellow, yellow ultramarine, zinc greens, cadmium yellows, cadmium red, cobalt yellow, the cinnabars, ultramarines, and Guignet greens. The cobalt violets, cobalt blues and cobalt greens appear to be almost entirely unchanged. Paris blues and Turnbull blues are decolorised with extraordinary rapidity; this light reaction is, however, reversible, like that of the unmixed Paris blues. That this accelerated action is due to the zinc white as such, and is not induced by the degree of dilution of the various pigments in question, is shown by the fact that equal percentage mixtures of the same pigments with lithopone, whiting, white lead and blanc fixe, exposed to light for the same length of time, underwent either only very slight alteration or none at all.

Further experiments showed that not only zinc white, but also zinc carbonate and hydrated zinc sulphide as well as cadmium carbonate, alter many pigments on exposure to light (*cf.* cadmium yellow).

Other less used artificial white pigments are: *Satin white*, which consists of a mixture of calcium sulphate and aluminium sulphate, *Manganese white*, *Strontium white*, *Tin white*, *Bismuth white*, *Tungsten white*, and *Antimony white*.

Lithopone.¹

(Charlton White; Zinc Sulphide White; Sulphide White; Enamel White; Griffith's patent Zinc White; Knight's patent Zinc White; Orr's White.)

The name "Lithopone," used in the widest sense, is applied to mixtures of zinc sulphide and zinc oxide with sulphates of the alkaline earths, particularly barium sulphate. The first technical preparation originated with Orr, who at first made zinc sulphide from barium sulphide and zinc chloride, and later prepared a mixture of zinc sulphide and strontium sulphate. Griffith's zinc white (1877) is a mixture of zinc sulphide and calcium or barium sulphate.

Meissner² prepared mixtures of zinc white and blanc fixe. The white pigment (zinc anhydride, zinc baryta) prepared by Alberti³ is of similar composition. The commercial products now known as lithopones are essentially mixtures of precipitated zinc sulphide and barium sulphate. In order to attain the necessary covering power for such a white lead substitute, each of the constituents should possess as good covering power as white lead itself; this, however, is not the case.

¹ Cf. *Le Blanc de Zinc et le Lithopone*, A. Souris, 1912.

² Ger. Pat. Nos. 4626 and 5926.

³ Ger. Pat. No. 80751.

The optical principle adopted in the preparation of lithopone for the purpose of securing the greatest possible covering power is as follows. An intimate mixture of two pigments of different refractive power is prepared in the amorphous form—not by mixing the dry constituents, but by precipitation—so that the differences of refraction of both towards air are as great as possible. Diffuse reflection of light as well as total reflection then takes place at the bounding surfaces of the grains more easily than would be possible in the case of a single pigment.

Mixtures of blanc fixe and zinc sulphide prepared by precipitation do not, however, possess sufficient covering power. The density of the pigment must therefore be increased by heating to redness, after which it is chilled in water in order to ensure the necessary fine state of division (fineness of grain). In the course of this process any free sulphur present in the precipitated mixture is burnt away and the zinc sulphide dehydrated. Meissner converted zinc sulphide completely into zinc oxide at white heat by means of high-pressure steam. At the present time the calcination of the pigment is no longer carried to the point at which the zinc sulphide is completely oxidised. Although the calcination process in the manufacture of lithopone results in the greatest possible covering power being obtained, there are also disadvantages connected with it. Part of the zinc sulphide is burnt to zinc oxysulphide, basic and neutral zinc sulphate and zinc oxide. Lithopone prepared from zinc chloride solutions produces zinc oxychloride. These constituents appear to be partly responsible for the want of permanence in light exhibited by the lithopones.

Lithopones prepared from pure materials (free from cadmium) possess a purer white tone than "chamber" white lead: they are non-poisonous and are not affected by hydrogen sulphide. When ground in oil they possess covering power equal to that of French white lead.¹ Many qualities are not pure white but greyish or more or less yellow, and they then contain carbon, iron, alumina, or cadmium oxide as impurities.

The more valuable and better covering component of these pigments is the anhydrous zinc sulphide, and they are, therefore, sold according to their content of this constituent.² With lithopone, as with zinc white, designation by "sealing" is used. In this case, however, the "sealing" does not refer to purely physical differences in quality, but to differences in the percentage amount of zinc sulphide, the latter forming

¹ Cf. J. F. Sacher, *Farben-Zeit.*, 1910, 15, 1543; 1911, 16, 542; and Meister, *ibid.*, 1910, 15, 1652.

² Cf. E. Kochs and E. Seyfert, *Z. angew. Chem.*, 1902, 15, 802; *J. Soc. Chem. Ind.*, 1902, 21, 1145.

the standard of value. A fixed amount of zinc sulphide corresponds to each seal, viz. :—

Green seal	33 per cent. ZnS and upwards
Red seal	30 " " (1 per cent. latitude)
White seal	26 " " (1 " ")
Blue seal	22 " " (1 " ")
Yellow seal	15 " " (1 " ")

In general, however, the sealing appears to be arbitrary, for a product containing 30 per cent. ZnS is sold from one factory as "red seal brand," and from another as "green seal," so that in this case, as in that of many other pigments, it is desirable to set up a series of standards. The different brands of lithopone are naturally of unequal covering power on account of the varying proportions of the two constituents.

Analysis.—In the analysis of lithopone, in addition to the main constituents, zinc sulphide and barium sulphate, secondary constituents dependent on the method of manufacture must be taken into account, viz.—zinc oxide, possibly zinc carbonate, zinc oxychloride, zinc oxysulphate and zinc sulphate; also barium carbonate and barium sulphide.¹ Technical impurities include ferric oxide, alumina, lime, magnesia, copper, and carbon. A qualitative examination for the constituents mentioned should precede the quantitative analysis.²

I. *Estimation of Zinc.* (a) *Gravimetric Method.*—P. Drawe³ recommends the following method:—The total amount of zinc present as sulphide, oxide, oxysulphide, etc., is first determined. For this purpose 1.0-1.5 g. of the finely powdered sample are weighed out into a beaker of about 200 c.c. capacity, agitated with 10 c.c. of hydrochloric acid (sp. gr. 1.19) and treated with a pinch of potassium chlorate; about half of the hydrochloric acid is then evaporated off on a boiling water-bath, the solution diluted with hot water, and treated with dilute sulphuric acid in order to increase the insolubility of the barium sulphate; the solution is then decanted off through a filter paper and the residue washed until the washings are no longer acid. The filtrate is heated to boiling in a porcelain dish of 500 c.c. capacity, over which an inverted funnel is placed, and, by the gradual addition of sodium carbonate solution, the acid is first neutralised, and the zinc then precipitated as carbonate. The precipitate is filtered off, washed, ignited, and the zinc weighed as oxide.

The estimation of the zinc present as sulphide is carried out by digesting 1-1.5 g. with 100 c.c. of 1 per cent. acetic acid in a beaker

¹ Cf. H. Wolff, *Farben-Zeit.*, 1910, 15, 1859; also, Austin and Keane, *Analyst*, 1912, 37, 238.

² Cf. C. Coffignier, *Bull. Soc. Chim.*, 1902, 27, [15] 829, [18] 943; *J. Soc. Chem. Ind.*, 1902, 21, 1146, 1377.

³ *Z. angew. Chem.*, 1902, 15, 174, 229, 297; *J. Soc. Chem. Ind.*, 1902, 21, 427.

at the ordinary temperature for about half an hour, then decanting through a small filter paper, and washing well with warm water. The residue on the filter paper is then added to the residue in the beaker, and the whole treated, as in the estimation of total zinc, with hydrochloric acid and potassium chlorate, etc. The zinc oxide so obtained gives the amount of zinc present as sulphide. The difference between the first and second estimations represents the amount of zinc present as oxide, carbonate, and oxysulphide.

Carbon dioxide and sulphuric acid, if present, are determined by the usual methods, and in the statement of results are taken as combined with zinc.

Barium sulphate can be estimated by direct weighing of the insoluble residue on treatment with hydrochloric acid.

E. Kochs and E. Seyfert¹ determine the zinc by precipitation with ammonium sulphide:—5 g. of lithopone are heated in a half-litre flask with 100 c.c. of hydrochloric acid (sp. gr. 1.12) until all the sulphuretted hydrogen is driven off; after cooling, the flask is filled up to the mark, 100 c.c. of the filtered solution, rendered alkaline with ammonia, are treated with ammonium or sodium sulphide at 50°-70°, and the precipitated sulphide ignited and weighed as ZnO. If, on the addition of ammonia, a precipitate of iron or aluminium is formed, then the weighed oxide of zinc is dissolved in hydrochloric acid and the contained iron and aluminium determined. In addition, the zinc salts soluble in acetic acid are also determined. For this purpose 5 g. of lithopone are shaken for some time with 100 c.c. of 5 per cent. acetic acid in a 250 c.c. flask at the ordinary temperature, the solution made up to 250 c.c., filtered through a double filter paper until a clear filtrate is obtained, and the zinc precipitated in 200 c.c. of the solution. It is stated that up to 12 per cent. of zinc carbonate or oxide may be detected in many qualities of lithopone.

J. S. Remington and C. Smith² recommend the following method of analysis as rapid, exact, and generally applicable. The sample is first tested for salts of iron, zinc, calcium, and barium soluble in water. A separate portion is tested for barium carbonate the percentage of which is determined, if necessary, by dissolving 2 g. in 50 c.c. of dilute hydrochloric acid, filtering, and precipitating the barium soluble in hydrochloric acid with dilute sulphuric acid. For the determination of the barium sulphate and zinc sulphide 0.5 g. of the sample is mixed with 25 c.c. of water at 40°, 0.5 g. of bromine added, the containing flask covered with a watch-glass, and set aside for one hour during which it is occasionally agitated; 10 c.c. of concentrated hydrochloric acid are then added, the excess of bromine expelled by heat,

¹ *Z. angew. Chem.*, 1902, **15**, 802; *J. Soc. Chem. Ind.*, 1902, **21**, 1145.

² *Caoutchouc et Gutta-Percha*, 1909, **6**, 3259; *J. Soc. Chem. Ind.*, 1909, **28**, 1049.

then 25 c.c. of water added, the contents of the flask boiled and filtered, and the residual barium sulphate washed, dried, ignited, and weighed. The filtrate is precipitated with barium chloride, and the barium sulphate formed is weighed; the proportion of zinc sulphide is then calculated from the weight of barium sulphate obtained.

For the determination of the total zinc, 0.5 g. of the sample is treated with hydrochloric acid, boiled until all the sulphuretted hydrogen has been expelled, a little dilute sulphuric acid added, the solution again boiled, and the zinc precipitated as carbonate and weighed as oxide. This, less the weight of zinc oxide corresponding to the zinc sulphide found, gives the content of zinc oxide. Should any barium carbonate have been found, the corresponding weight of barium sulphate must be deducted from the weight of the total barium sulphate (estimated as such), and added to the weight of barium sulphate corresponding to the zinc sulphide. If salts of iron, calcium, or barium are present in the solution containing the zinc, these must be separated by ammonia and ammonium sulphide. Analyses of 12 average samples of English lithopone are given in the paper; in these the percentage of barium sulphate varies from 58.16-80.80, that of zinc sulphide from 21.54-33.92, that of zinc oxide from 0.28-3.36, and that of barium carbonate from nil to 0.98.

(b) *Volumetric Method*.—H. Amsel¹ uses the following method:—50-75 c.c. of the hydrochloric acid solution, filtered from barium sulphate, are treated with 1 c.c. of 10 per cent. ferric chloride and 20 c.c. of a 40 per cent. solution of neutral potassium tartrate; the solution is then neutralised with ammonia and boiled. If the solution is not clear more ammonia is added. The solution is then treated with a standard solution of calcium ferrocyanide until all the zinc is precipitated, this being recognised by bringing together a drop of the solution and a drop of strong acetic acid on a white porcelain plate, when a blue coloration (Prussian blue) is immediately produced. The zinc oxide or carbonate is estimated separately by extracting with 5 per cent. acetic acid. The volumetric method of estimating zinc in lithopone has the advantage of rapidity.

II. *Estimation of Zinc Sulphide by determining the Sulphur present as Sulphide*. (a) *Gravimetric Method*.—P. Porth² carries out this estimation according to Jannasch's method by heating the lithopone in bromine vapour and collecting the resulting sulphur bromide in dilute hydrochloric acid. The bromine is conducted over the lithopone, contained in a boat in a glass tube, by means of a stream of carbon dioxide.

When barium sulphide, which occurs extremely rarely in lithopone, is present, J. F. Sacher³ recommends that the sample be extracted with

¹ *Z. angew. Chem.*, 1902, 15, 174. ² *Farben-Zeit.*, 1909, 14, 1986. ³ *Ibid.*, 1910, 15, 1810.

water, before estimating the sulphur present as zinc sulphide. The sulphide-sulphur is then estimated by treatment with metallic tin and hydrochloric acid, and passing the evolved hydrogen sulphide into an ammoniacal hydrogen peroxide solution; the resulting sulphuric acid is then precipitated with barium chloride. The apparatus used consists of a cylindrical glass vessel about 20 cm. long and 2 cm. wide which can be hermetically closed by means of a glass stopper provided with a two-way cock in connection with a gas inlet and outlet tube and a funnel tube. On to this the absorption tube containing ammoniacal hydrogen peroxide is connected. In carrying out the determination 1-2 g. of the purest tin, then the weighed substance (0.5-1 g.) packed in tinfoil, and over this another layer of tin are successively placed in the apparatus, concentrated hydrochloric acid is run in through the funnel, the vessel closed by turning the tap, and heated in an oil-bath to the boiling point of the hydrochloric acid. When the tin is dissolved, the decomposition vessel is connected with a hydrogen apparatus and the last traces of hydrogen sulphide are driven over into the absorption vessel.

In connection with the estimation of barium sulphate in the residue Sacher suggests a correction, as the results, in consequence of partial solution of that substance in the hydrochloric acid solution of stannous chloride, come out about 0.7 per cent. too low. He transfers the contents of the decomposition vessel to a flask and dilutes with water to 300 c.c., adds a few cubic centimetres of 10 per cent. barium chloride solution, boils, and allows to stand for a considerable time in the cold.¹

(b) *Volumetric Method*.—H. Wolff² directs attention, in the first place, to the sources of error in the method of estimating the content of zinc by difference, and then to the inconvenience of precipitating zinc as sulphide and carbonate. In the latter case, whenever calcium is present (in lithopone "yellow seal"), it is precipitated with the zinc. He therefore recommends the precipitation of the latter with hydrogen sulphide from a weakly acid solution. In contrast to this, the methods depending on the oxidation of sulphide-sulphur have the advantage of being direct methods. At the same time, connected with the latter is the disadvantage that if sulphates (zinc sulphate, gypsum) are present the estimation of the already existing sulphuric acid is rendered necessary, and these methods thereby become indirect. These disadvantages are overcome by volumetric estimations, using iodometric methods. Wolff removes any barium sulphide present by boiling the weighed sample with 2 per cent. acetic acid. After this treatment the lithopone is mixed with 0.5-1 g. of sodium carbonate in a 200 c.c. flask

¹ Cf. *Chem. Zeit.*, 1909, 33, 941; *J. Soc. Chem. Ind.*, 1909, 28, 1066.

² *Farben-Zeit.*, 1910, 15, 1859.

fitted with a tap-funnel and delivery tube, and hydrochloric acid is added through the funnel. The carbon dioxide evolved displaces the air and prevents oxidation of the hydrogen sulphide. On boiling, the latter is driven over into the receiver of two Peligot tubes containing respectively 50 c.c. and 2-3 c.c. of $N/14$ iodine solution. After combining the two solutions the excess of iodine is titrated back with $N/14$ thiosulphate solution. 1 c.c. iodine solution used corresponds to 4.873 mg. zinc sulphide. In the control estimations, or in the first estimation provided that the zinc-content of the sample is known approximately, the 50 c.c. of iodine solution are divided, instead of placing the whole amount in the Peligot tubes, and a sufficient quantity is introduced into the generating flask to ensure the decomposition of some nine-tenths of the hydrogen sulphide at the moment of formation. A large excess of iodine (with lithopone "red seal" 0.3-0.4 g.) is used.

This method has the advantage of being rapidly carried out and, according to Wolff, gives more reliable results than those obtained by the double zinc estimation, especially when zinc oxychloride is present, as the latter, even with 5 per cent. acetic acid, is not dissolved without leaving a residue, but only on boiling with 10-15 per cent. acid. In this case, and also when *oxysulphates* are present, the method of double zinc estimation gives values up to 2 per cent. too low.

In order to obtain a correct idea of the composition of lithopone and especially of the distribution of the zinc, Wolff recommends that in the qualitative analysis the substance be treated successively with cold and then hot 3 per cent. acetic acid, with hot 10 per cent. acetic acid, and finally with hydrochloric acid.

W. L. Austin and C. A. Keane¹ recommend the estimation of the total zinc volumetrically and that of the zinc sulphide indirectly by oxidising the sulphide-sulphur to sulphate. The gravimetric estimation of the zinc as carbonate is inaccurate in presence of calcium and iron, both of which are usually present, and its precipitation as sulphide is a lengthy determination. They regard the oxidation and subsequent precipitation of the sulphide-sulphur as simpler and easier to carry out than the determination of the hydrogen sulphide evolved on decomposition.

For the volumetric estimation of the zinc a method devised by A. Voigt² for the analysis of zinc ores and products was employed which is sufficiently accurate for the estimation, and which has the advantage that the results are not affected by the presence of iron or calcium. For the oxidation of the sulphide-sulphur either bromine or nitric acid may be used; the former was found preferable, and the estimation is carried out on the same lines as proposed by Remington and Smith.

¹ *Analyst*, 1912, 37, 238.

² *Z. angew. Chem.*, 1889, 2, 307.

This combination was found more rapid and adaptable than previous proposals, and sufficiently accurate for technical purposes.

The method of analysis is as follows:—5 g. of the finely ground sample are treated with concentrated hydrochloric acid and a little potassium chlorate, the whole evaporated to a small bulk on the water-bath, taken up with boiling water, and the residual barium sulphate filtered off and thoroughly washed. The filtrate is collected in a 250 c.c. graduated flask, made up to the mark, and aliquot portions taken for the estimation of the total zinc by Voigt's method. The potassium ferrocyanide solution is made up by dissolving 46 g. of the crystallised salt in a litre of water, and is standardised by a solution of zinc chloride containing 12.4476 g. of pure zinc oxide per litre; 1 c.c. of this solution is equivalent to 0.01 g. of zinc. For the estimation, 50 c.c. of the above filtrate are taken, 10 c.c. of a solution of tartaric acid (200 g. per litre) and 10 c.c. of a solution of ferric chloride (60 g. per litre) added, the whole diluted to about 200 c.c., made just alkaline with ammonia, and titrated; the completion of the reaction is determined by adding a drop of the solution to dilute acetic acid (1 : 3) on a pitted porcelain plate until a permanent blue colour is produced. After a preliminary estimation a sharp end-reaction is easily secured, and it is not affected by the presence of an excess of ammonia. In a series of tests made, in which the quantity of ammonia added was increased up to twice the amount necessary for neutralisation, the maximum difference in the titrations did not exceed 0.15 c.c.

For the estimation of the sulphide-sulphur, 0.5 g. of the sample is oxidised with bromine, after the addition of water, hydrochloric acid added, the residual barium sulphate filtered off, and the sulphuric acid in the filtrate precipitated by barium chloride. By calculating the sulphur thus found to zinc sulphide, and subtracting its equivalent of zinc from the total zinc estimated volumetrically, the content of zinc, other than sulphide, is obtained by difference, as stated above.

III. *Barium Sulphate* is estimated directly by weighing the residue obtained on decomposition of the lithopone with hydrochloric acid, bearing in mind the partial solubility of barium sulphate in the latter (Wolff). In addition, the estimation of moisture, which should not amount to more than 0.2-0.3 per cent., must be carried out.

Fastness to Light.—The question as to the permanence of lithopone in light acquires special practical importance in view of the observations made with regard to the action of zinc white on pigments in the light. Lithopone turns grey in the light, as Phipson observed so long ago as 1880. The reaction is reversible and takes place more feebly under glass. It is therefore caused partly by ultra-violet rays.¹ The components of lithopone responsible for this lack of permanence in light

¹ In opposition to this view, cf. O. Lehmann, *Molecularphysik*, 1888, vol. i., 240.

do not yet appear to be known. It is attributed partly to the presence of soluble salts of zinc and of other metals,¹ partly to zinc sulphide, in the hydrated form,² and partly to zinc oxide and basic zinc salts. According to Ostwald, the grey coloration of lithopone behaves as if it proceeded from finely divided metallic zinc.³ Whether this reversible light-reaction can become partly or entirely irreversible has not yet been established.

Behaviour of Lithopone in Mixtures with Pigments containing Lead.—The stability of varieties of lithopone towards white lead appears to depend on their quality. A mixture of lithopone "green seal" and white lead free from acetate, mixed in water and allowed to settle, showed no change of shade in two years, whereas another mixture containing an inferior quality had become black in spots on the side exposed to the light in fourteen months. Thus even in the latter case no chemical reaction in the real sense took place, but only a reaction accelerated locally by the action of light. It was observed that when pale mixtures of lithopone "green seal" with coal-tar dyes were exposed to the light, the lithopone did not injure the permanence of such mixtures as zinc white did, but diminished it probably just as little as whiting, heavy spar, and white lead would have done. On the other hand, instances of such mixtures turning grey have been observed repeatedly. Thus it appears that non-genuine lithopone still comes into the market.

*Steinau's Sulfopone*⁴ is obtained by treating a solution of calcium sulphide with a solution of zinc sulphate at 44°, and heating the resulting mixture of zinc sulphide and calcium sulphate to 250°-300°. For some years white pigments have been prepared from artificial zinc sulphide. According to J. C. A. Meyer of Lyons, this possesses even greater covering power than white lead. He found that if lead salts (about 2 per cent.) are present, the iron in zinc lyes comes down with the lead on treatment with hydrogen sulphide, and thus pure zinc solutions are obtained for precipitation with hydrogen sulphide. The precipitated zinc sulphide is then dehydrated.⁵ A very finely divided and therefore good covering zinc sulphide was obtained by de Stucklé,⁶ by precipitation from a mixture of metallic zinc and caustic baryta solution, hydrogen being evolved at the same time; or by precipitation of zinc sulphide at the negative electrode of an electrolytic bath.⁷

¹ Alberti, R. Steinau, Ostwald, and Brauer.

³ Church-Ostwald, *Farben und Malerei*, p. 147.

⁵ Ger. Pat. 192531, 25th August 1906.

⁶ Ger. Pat. 167172, 19th February 1904.

⁷ Ger. Pat. 167498, 14th August 1904; cf. also, Ger. Pat. 171872, 23rd March 1904.

² de Stucklé.

⁴ Ger. Pat. 74591.

III. GREY PIGMENTS.

(Slate Grey ; Stone Grey ; Silver Grey ; Mineral Grey.)

Slate grey is obtained by grinding and levigating special kinds of grey slate which occur in several parts of Germany, chiefly in the Eifel and near the Rhine. It is a fine yellowish- or reddish-grey powder which, on account of its property, as an oil colour, of drying very hard, is used for priming paint and for the preparation of putty. It is frequently imitated by means of a mixture of white clay, black, ochres and ultramarine.

Zinc Sulphide Grey, Zinc Blende, Calamine White.—Under these names powdered dense zinc blende has been sold for a considerable time for industrial oil painting, especially of iron bridges, etc. It is also artificially made up by tinting lithopone, etc., with charcoal black, ultramarine, and ochres, in order to obtain the light yellowish-grey tint of natural zinc sulphide grey. The latter can easily be distinguished from such preparations, for on treatment with hot hydrochloric acid it does not at first noticeably change its tint, whereas in the case of the artificial products the tint becomes changed owing to the decomposition of the ultramarine. On further heating, the natural product dissolves completely or leaves a slight residue of silica, and hydrogen sulphide is vigorously evolved ; with the substitutes, however, barium sulphate mixed with carbon remains behind.

Zinc Grey.

This name was originally used for the *Zinc Dust* obtained on smelting zinc ores, and containing about 98 per cent. of metallic zinc. It dries hard in oil and is therefore particularly adapted for use as a paint on iron ; it also preserves the iron from rust. Substitutes for this comparatively expensive colour are prepared from grey zinc oxides, which owe their colour to the presence of carbon, and are waste products in the manufacture of zinc white. They come into the market under such names as *Diamond grey, Silver grey, Platinum grey*, and they are also prepared artificially as mentioned under "zinc sulphide grey." They are distinguished from genuine zinc grey by the difference in specific gravity ; also by estimating the zinc-content, or by proving the presence of a residue insoluble in acids.

IV. YELLOW PIGMENTS.

The Yellow Ochres.

(Ochre ; Yellow Earth ; Oxide Yellow ; Chinese Yellow.)

The typical natural varieties of ochre are disintegration products of ferruginous minerals of which felspar is a constituent. The latter is broken down into clay in process of weathering. The ochres there-

fore represent clays coloured by ferric oxides, and thus belong to the class of natural substratum colours. The hue of the ochres depends respectively on the amount of ferric hydroxides contained, and on the presence of slight amounts of oxides of manganese (dark ochre). The typical ochres must be distinguished from the siennas. The former, owing to their content of clay, possess more or less body; the latter, on account of the low content or absence of clay and the high water-content of the colouring principle, are glazing colours, and it is accordingly incorrect to include them with the ochres. The covering power of the natural and also of the artificial ochres (see Mars yellow) is, moreover, dependent on the degree of hydration of the ferric oxide present. Hydrated ferric oxide does not occur in nature exclusively as the ortho-hydrate $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O}$, which possesses the highest glazing power. The colour of the ochres varies, according to the content of clay, the degree of hydration of the ferric oxide and the admixture of manganese oxides, from palest yellow through golden yellow to brown-yellow.

The preparation of ochres for use as paints, artists' colours, etc., is confined to the processes of crushing, levigating, sieving, drying, grinding, etc. Only the finest qualities are employed for artists' use. Standards of purity as employed in the case of artificial mineral ground-colours cannot be used in valuing ochres, for, apart from the exceptions mentioned, they are varying mixtures of the colouring components and the substratum. Accordingly the chemical analysis is confined to the identification of the components of the mixture, and only in special cases is a determination of the quantitative composition of value.

All ochres, especially those for use as paints, do not come into the market in the "naturally genuine" condition. The more brownish varieties particularly are rendered lighter in colour by the addition of white substrata such as heavy spar, whiting, blanc fixe, and lithopone, and more brilliant by the addition of chrome yellow.¹

Analysis.—The qualitative analysis of the ochres comprises chiefly tests for the presence of bituminous constituents, of basic sulphates, and of whiting. By heating the sample in a sealed tube, bituminous matter is readily recognised, and an acid reaction of the water given off indicates the presence of basic sulphate; whiting is tested for by treatment with hydrochloric acid. The presence of whiting in ochres is disadvantageous in so far that in the burnt condition they have then little durability as oil colours, especially for painting in the open air, for the caustic lime which is formed acts on the oil, giving a soap which is easily hydrolysed by water, whereby the paint is quickly destroyed. Baryta also occurs in exceptional cases as an accessory

¹ Cf. Zerr and Rübencamp, *Colour Manufacture*, p. 385.

component of the ochres. In the burning process the colour of the ochres changes to red owing to the formation of ferric oxide, and the shade varies according to the content of iron and manganese respectively. At the same time the covering and drying power as an oil colour is increased.

Siennas.

(Terra de Siena ; Italian Earth ; Mahogany Brown ; Cashew Lake.)

All these earths are distinguished from the typical ochres by their high content of iron and of water, and by the absence or marked relative decrease in the amount of clay, the place of which is taken by silica. Outwardly they also differ from the earthy and powdery ochres since they form yellow-brown to dark brown hard lumps with a conchoidal fracture. For the purpose of distinguishing between the siennas and the typical ochres, equal quantities of each are boiled with concentrated hydrochloric acid until they are decomposed, the solutions are made up to the same volume with water, and allowed to settle. The siennas then form deep yellow to brown-yellow solutions, containing a relatively small semi-transparent gelatinous sediment (silica); the ochres form light yellow solutions containing a copious opaque white sediment (clay).

Mahogany brown is a sienna which has been ignited, ground wet, made up in the form of pieces, and dried. Cashew lake is a similar brown on to which organic dyes are precipitated.

The siennas are chiefly used as glazing colours in artistic and decorative painting, and especially for lacquering wood. Their covering power, like that of the ochres, is improved by calcining. The stability of ochres and siennas to light and air is unlimited, and this is also true as regards miscibility.

The darkening of ochres, and especially of unburnt sienna in oil, probably arises from their slight solubility in fatty oils, or from the gradual decrease in water-content of the hydrated ferric oxides, from which darker coloured lower hydrates result.

The Examination of Mineral Colours for Arsenic.—C. Fischer,¹ in examining mineral colours for arsenic, made use of the method of Mayrhofer, in which arseniuretted hydrogen is evolved and led into an *N*/100 silver nitrate solution, and the excess of silver titrated back with *N*/100 thiocyanate solution. Out of 27 commercial samples examined, 13 gave no arsenic mirror in Marsh's apparatus, 10 gave a faint, transparent mirror indicating under 0.01 per cent. As_2O_3 , and 4 gave a strong opaque mirror. Methods for the approximate estimation of small quantities of arsenic are fully described in Vol. I., pp. 362 *et seq.*

¹ *Chem. Zentr.*, 1903, I., 995.

Artificial Ochres.

(Mars Yellow ; Siderin Yellow.)

These yellow iron colours are prepared, according to one method, by dissolving ferrous sulphate in water so as to obtain a solution of sp. gr. 1.06, warming in earthenware vessels, and introducing strips of sheet zinc. The precipitate which separates out forms, after being washed and dried, a bright yellow ochre-coloured and extraordinarily delicate powder similar in tone to dark Naples yellow. Darker rust-yellow varieties are said to be obtained by using ferric chloride in place of ferrous sulphate. According to another process a solution containing equal parts of ferrous sulphate and alum is treated with sodium carbonate, the mixed aluminium and iron precipitate is thoroughly washed, and dried at a moderate temperature. According to Mierzinski, the precipitate, if prepared according to these directions, must contain hydrated ferrous oxide, and can only produce the yellow colour on oxidation in the air. These pigments are evidently partially hydrated ferric oxides; hence their covering action. By calcination artificial ochres are obtained which are known under the names of *Mars orange*, *Mars purple*, and *Mars violet*. The colours prepared according to the first method contain zinc; the others contain alumina. They are dearer than the natural ochres, and they are used almost solely as artists' colours. They should not contain any basic sulphates. A bright orange-yellow colour which is a basic ferric chromate is sold under the name of *Siderin yellow*. It is described by Mierzinski as particularly applicable for water-glass painting. It is, however, little used. Nothing disadvantageous is known as regards the permanency in light and compatibility of these pigments.

Realgar (As_2S_2).**Orpiment** (As_2S_3).

(King's Yellow.)

These naturally occurring sulphides of arsenic are also obtained as by-products in the roasting of arsenical pyrites. They are characterised by their poisonous properties, sensitiveness to light, and incompatibility with certain other colours, and are easily recognised by their volatility on being heated alone, and by the arsenical odour evolved when heated on charcoal.

Naples Yellow.

(Antimony Yellow ; Paris Yellow.)

Naples yellow is essentially basic lead pyro-antimonate with varying quantities of lead oxide or free antimonious acid. Neutral lead antimonate

is white and becomes yellow when heated, owing to conversion into the pyro-antimonate.

Two varieties are prepared, viz., light and dark. The colour of light Naples yellow, if arising from excess of lead oxide, can be improved by treatment with dilute nitric acid. The tone of Naples yellow depends not only on the proportions in which the components are mixed, but also on the temperature employed, and stands in inverse ratio to the latter. The pigment, therefore, does not possess a constant percentage composition. The lighter varieties prepared with zinc oxide, etc., and the chief coloured component of which is lead pyro-antimonate together with lead oxide, are applicable as substrata. Besides lead and antimony all genuine Naples yellows contain varying quantities of chlorine present as basic lead chloride (Mineral yellow, Turner's patent yellow, Cassel yellow), which does not, in this case, constitute an addition or adulteration. It results, rather, from the reaction of the flux—viz. common salt—with the lead compound which serves for the preparation of the colour.

Analysis.—For the purpose of identifying and estimating the chief components, Naples yellow is fused with sodium carbonate and sulphur, and the melt extracted with water. The black residue contains the lead as sulphide and the zinc if present. The yellow solution consists of sodium thio-antimonate, possibly mixed with sodium thio-stannate. The lead, zinc, and antimony are separated and estimated by the ordinary analytical methods.

In rare cases adulteration of Naples yellow with chrome yellow or chrome orange occurs. On warming the colour with hydrochloric acid a green solution is obtained in this case.

The shade of genuine Naples yellow has been imitated by mixing orange-coloured cadmium yellow with zinc white, or more rarely with white lead. The use of this mixture as an artists' colour, and especially as a water colour, is inadvisable on account of the properties of zinc white mentioned above (p. 923).

A pigment related to Naples yellow was formerly made under the name of *Antimony yellow*, which was a mixture of oxychlorides of bismuth and lead with lead antimonate.

Genuine Naples yellow is a strong body colour, completely stable as regards weather conditions, and therefore applicable as a lime colour. It is also stable on ignition, and is therefore applicable for painting on glass and porcelain. On the other hand, like all lead pigments it is affected by hydrogen sulphide, but the coloration disappears again on exposure to light, or on treatment with hydrogen peroxide. On account of its relatively high price Naples yellow is chiefly used as an artists' colour.

It is quite fast to light, but mixtures of Naples yellow with zinc yellow, baryta yellow, or zinc green gradually darken.

Cassel Yellow.

(Mineral Yellow ; Veronese Yellow ; Turner's Yellow.)

Cassel yellow is a basic lead chloride of varying composition, frequently corresponding to the formula $\text{PbCl}_2 + 7\text{PbO}$. For its preparation 10 parts of red lead and 1 part of sal-ammoniac are heated to fusion; metallic lead separates out at the bottom of the crucible, while the yellow oxychloride forms above. A Cassel yellow containing alumina, and used as an enamel, is prepared by heating together equal parts of white lead, sal-ammoniac, and alum in a crucible. Chrome yellow has to a large extent superseded Cassel yellow.

The proportion of lead chloride to lead oxide, a frequently varying figure, is determined by dissolving the colour in dilute nitric acid and a large quantity of warm water, care being taken to prevent evolution of chlorine. Silver nitrate is then added to the solution, and from the weight of silver chloride obtained the amount of lead chloride present may be calculated.

Tungsten Yellow.

This consists of tungstic acid and is prepared by decomposing wolframite with sodium carbonate, reacting on the alkali tungstate with calcium chloride, adding the resulting calcium tungstate to warm hydrochloric or nitric acid, and washing the precipitated tungstic acid. Tungsten yellow is either fiery lemon-yellow in colour with a greenish cast, or orange-yellow, according to the manner in which it is purified. It becomes faintly green on exposure to light, a change said to be due to the alkali it contains.¹

Litharge and Massicot.

Yellow oxide of lead is now seldom used as an independent colour, and, as massicot, serves principally as the raw material for the preparation of red lead.

Litharge is obtained as a by-product in the process of smelting silver, and differs from *Massicot* by its more reddish colour. According to Zerr and Rübencamp, it is to be looked upon as fused and crystalline lead oxide which must first be converted into the pulverulent commercial form by grinding. Litharge is unsuitable for the preparation of red lead, as it can only be further oxidised with difficulty.

The preparation of massicot is carried out in specially constructed reverberatory furnaces in which oxidation of the lead can take place without fusion of the resulting oxide, and which permit of the latter being obtained in the finest possible state of division, a condition

¹ Mierzinski, *Handb. der Farbenfabrikation*, 1898, vol. i., p. 426.

favourable for the subsequent oxidation to red lead. (*Cf.* Red Lead, p. 957.) The preparation from white lead is now no longer usual.

The analysis of litharge is described in the section on "Metals other than Iron," Vol. II., p. 238.

Uranium Yellow.

This pigment is prepared by roasting pitchblende with sodium carbonate and potassium nitrate, whereby soluble uranyl sodium carbonate is obtained, which, after removal of impurities by means of sodium carbonate, is neutralised with sulphuric acid, when uranium yellow is precipitated out in the form of a delicate light yellow powder. It is a hydrated sodium uranate corresponding to the formula $\text{Na}_2\text{U}_2\text{O}_7 + 6\text{H}_2\text{O}$.

On addition of caustic soda to the solution of the uranyl sodium carbonate obtained as described above, a precipitate of darker colour is produced known as *Orange-coloured Uranium yellow*. On ignition it passes into anhydrous *Dark Orange-coloured Uranium yellow*. The uranium colours are chiefly used for porcelain painting and for the preparation of uranium glass, which is characterised by its green fluorescence.

Cadmium Yellow and Cadmium Orange.

Cadmium yellows are sold in different shades under the designations lemon, pale, medium, dark and orange, or as Nos. 0-6 and 1-7 respectively, the lowest figure denoting the palest tone. As regards the preparation and chemical composition of the commercial varieties of cadmium yellow, there are few definite statements even in the latest literature. They are obtained in the wet way either by passing hydrogen sulphide into solutions of cadmium salts or by precipitating with alkali sulphides, and also in the dry way by strongly heating cadmium carbonate with sulphur; and to some extent the various shades obtained by these different methods are under the control of the manufacturer. It is frequently maintained that all varieties of cadmium yellow prepared in the wet way are, without exception, pure cadmium sulphide (CdS). The older assumption of H. Schiff,¹ according to which cadmium formed an ascending series of sulphur compounds, amongst others a pentasulphide, was disproved by O. Follenius² and by G. Buchner.³ Further, Follenius also found that on passing hydrogen sulphide into solutions of cadmium salts, chemically pure cadmium sulphide could not be obtained, as it always contained up to 2 per cent. of the cadmium salt from which it was precipitated. These technical accessory components of cadmium

¹ *Annalen*, 1860, **115**, 74.

² *Z. anal. Chem.*, 1874, **13**, 411.

³ *Chem. Zeit.*, 1887, **11**, 1087, 1107.

sulphide cannot be removed by washing, and (like the red lead sulphochloride, etc.) they are either present as double salts or else are adsorption mixtures with the cadmium sulphide. On ignition this impurity volatilises as a simple cadmium salt and forms a white efflorescence, leaving pure cadmium sulphide behind.

The shades of technically pure, unadulterated cadmium sulphides depend on the manner of preparation. All cadmium sulphides prepared in the dry way and those prepared in the wet way and subsequently ignited have approximately the same shade, a very pale golden yellow with a dull ochre-yellow tint; the purple-red discoloration which appears on ignition disappears on cooling, and is therefore attributable to similar physical causes as the turning yellow of zinc oxide, the darkening of mercuric oxide when heated, etc. Their hue is not identical with that of the lightest varieties prepared in the wet way, *e.g.* "Cadmium lemon" or Nos. 0-1. When the preparation is carried out by treating solutions of cadmium salts with alkali sulphides, usually only a dull orange-yellow sulphide is obtained. The orange-coloured precipitate (probably oxysulphide) often obtained at first rapidly changes, on standing, into light golden yellow, which becomes orange on drying. The pigment so obtained is not cadmium sulphide (CdS) but probably the hydroxy-hydrosulphide $\text{Cd}(\text{SH})(\text{OH})$.¹ This variety of cadmium yellow possesses the property of passing into the colloidal state. The precipitates obtained by treating solutions of cadmium salts with hydrogen sulphide either at ordinary temperatures or hot, in presence of excess of acid, deepen in colour, according to concentration, temperature, and amount of acid in the solutions, from palest whitish-yellow and lemon at first up to deep orange-yellow, and this takes place even during the passing in of the hydrogen sulphide and also on washing. The only stable tones obtained, after drying the precipitate, are a deep golden yellow and a pale orange-yellow respectively. The palest lemon- and golden yellow cannot be obtained in the dry state by this method.

The causes of the colour change of cadmium sulphide precipitated by hydrogen sulphide have been investigated by A. H. Church (1876), G. Buchner (*loc. cit.*, 1887), A. W. Keim, N. von Klobukow,² K. Haushofer³ and T. Niederländer.⁴ It was found, amongst other data, that the specific gravity of the paler varieties of cadmium yellow amounted to 3.9-4.5, and that of the dark varieties 4.5-4.8, a variation similar to that observed in the case of natural cadmium sulphide, Greenockite (4.5-5.9). Further, it was shown by Haushofer that all artificially prepared cadmium yellows are crystalline, and, with one exception (monoclinic), belong to the hexagonal system. N. von

¹ A. Eibner, *Farben-Zeit.*, 1908, 13, 1511, 1549.

² *J. prakt. Chem.*, 1887, 39, 412.

³ *Ibid.*

⁴ *Techn. Mitt. f. Malerei*, 1893, 10, 424.

Klobukow regards the differently coloured modifications of cadmium sulphide as due to isomerism, whilst G. Buchner attributes the differences to polymerism; the latter distinguishes between a pale yellow α , and an orange-yellow β modification. The observations made by W. Ostwald on precipitated and crystallised mercuric oxide render it, however, very probable that the variations in colour are due to varying size of grain.

The Pale Commercial Varieties of Cadmium Yellow.

None of the varieties of palest cadmium yellow is technically pure cadmium sulphide, which contains 77.8 per cent. of cadmium and 22.2 per cent. of sulphur. In the older of these pigments large quantities of zinc (up to 16 per cent.) were found; moreover, cadmium chloride, etc., was present up to 18 per cent. In the more modern products up to 59 per cent. of cadmium oxalate, or 68 per cent. of cadmium carbonate is found, while the cadmium sulphide content diminishes to 36.13 per cent. At the same time considerable quantities of water, and, frequently, ammonia are present.¹ These varieties, therefore, contain white substrata, the older having zinc as a basis, the newer German varieties, which are free from zinc, having cadmium oxalate or carbonate. The older French and German cadmium pigments, which contain zinc in the form of hydroxide or hydroxy-hydrosulphide, are of less monetary value than the newer kinds prepared from cadmium oxalate or carbonate, and are less stable than the latter, a defect probably connected with the greater instability of zinc hydroxy-hydrosulphide (tendency to oxidise). These varieties have, however, been almost completely superseded by the newer kinds.

Qualitative Analysis.—For the purpose of testing both these varieties qualitatively, A. Eibner heats a portion in a glass tube. If a strong bright metallic mirror quickly appears, then cadmium oxalate is present, which, on decomposition, gives metallic cadmium. Preparations containing cadmium carbonate give a faint mirror only after long heating. Carbon dioxide is identified by warming a portion of the substance with dilute sulphuric acid. Cadmium colours containing zinc are recognised by extracting with warm acetic acid and testing the filtrate with ammonium sulphide.

According to G. Buchner,² technically pure cadmium yellow should react as follows: (1) It should dissolve on warming with dilute hydrochloric acid to a clear and colourless solution (absence of free sulphur, heavy spar, and chrome yellow). (2) It should not contain any components soluble in water. (3) After agitation with acetic acid it should give a filtrate in which no cloudiness or precipitate is produced

¹ Cf. Eibner, *Malmaterialienkunde*, p. 134.

² *Chem. Zeit.*, 1887, **II**, 1087, 1107.

by potassium hydroxide (absence of any considerable quantities of zinc compounds or cadmium salts [substrata]). (4) Heated in a tube or on platinum foil it should become purple-red, and on cooling pure yellow again, but not brownish-yellow (absence of cadmium hydroxy-hydrosulphide or carbonate). (5) After agitation with ammonium hydroxide it should give a filtrate which is not coloured yellow by hydrochloric acid (absence of arsenic compounds). (6) Heated in a tube it should not give off any considerable amount of water, or ammonia instead of sulphur dioxide, and according to Eibner should not produce a metallic mirror (absence of cadmium and zinc hydroxy-hydrosulphides, and cadmium oxalate and carbonate as substrata). Technically pure cadmium yellow prepared in the wet way gives off only traces of water and sulphur dioxide when heated in a tube. A thin white deposit always forms above the substance, and is due to the sublimation of the cadmium salts (chloride, sulphate), which are carried down with the sulphide precipitate and cannot be removed by washing.

Quantitative Analysis.: (a) *Technically Pure Commercial Varieties.*—If the qualitative analysis establishes the fact that a cadmium substratum pigment is not being dealt with, then, for the purpose of separating cadmium from zinc, the substance is dissolved in hydrochloric acid, the cadmium precipitated by hydrogen sulphide and estimated as sulphide, after igniting with sulphur in a current of hydrogen; or the cadmium sulphide is converted into sulphate and weighed as such. By sublimation, or by boiling the colour with sodium carbonate solution, the amounts of cadmium chloride or sulphate present can be determined by difference.

(b) *Substratum and Adulterated Varieties of Cadmium Yellow.*—In this case the analytical procedure is determined according to the results of the preliminary qualitative examination. Estimations of the following substances are also involved: water, carbon dioxide, oxalic acid, sulphur, ammonia, and hydrated oxides of zinc and cadmium. The latter are extracted with dilute acetic acid, and estimated as described above. Adulteration with heavy spar, chrome yellow, etc., has very seldom to be considered in the case of cadmium yellow.

Properties.—The technically pure varieties of cadmium yellow (medium, dark, and orange) are pronounced body colours. On the other hand, the palest varieties, since they contain substrata of only low refractivity, are much inferior to the former in covering power. Cadmium hydroxy-hydrosulphide, in contrast to anhydrous cadmium yellow, is a pronounced glazing colour. In addition to these an orange-yellow hydroxy-sulphide, $\text{Cd}_2\text{S}(\text{OH})_2$, has been prepared by Buchner.

Fastness to Light.—Only those commercial varieties of cadmium yellow which consist of technically pure cadmium sulphide are fast to

light when in the form of powder and in water colour washes, so far as experiments with this comparatively new pigment have demonstrated up to the present. On the other hand, all cadmium substratum colours in powder form and in water colour washes are fugitive in light; the most fugitive are those rich in zinc. In powder form they fade (formation of white basic sulphates), while in water colour washes a change of colour to greenish-brown appears first of all; later they become bleached. The causes of this colour change are unexplained. In addition, cadmium hydroxy-sulphide (Buchner), glazing cadmium yellow, cadmium hydroxy-hydrosulphide (Eibner), and the substances prepared by precipitation with alkali sulphide and containing sulphur, are fugitive in light.

Behaviour in Mixtures (Fastness to Zinc White).—Cadmium yellow reacts with arsenic greens to form copper sulphide, but there are no statements in the literature regarding the vehicles in which this phenomenon appears most strongly, or as to whether all varieties of cadmium yellow exhibit it to the same extent. It was found that, as oil colours, the darker to orange-coloured varieties, including cadmium red, underwent almost immediate double decomposition with Schweinfurth green, while the paler and palest brands remained unchanged for a comparatively long period. As water colours the cadmium yellows react much less rapidly. The causes of this phenomenon are obviously to be found in the sensitiveness of the arsenic greens towards oil, the comparatively large amounts of pigment in the dark cadmium yellows, and the optically darkening action of the oil vehicle. Mixtures of "dark" cadmium yellow with chrome yellow and zinc green become deeper in shade, while it has been observed that mixtures of white lead with cadmium "lemon" and cadmium "dark," kept under water, remained unchanged for a year in a test under searching conditions; after three years' blackening had set in in the case of the former. After five years in oil no change was noticeable in any instance.

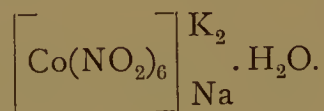
Both the cadmium substratum pigments and the technically pure cadmium sulphides fade with comparatively great rapidity when mixed with zinc white. A 1 per cent. mixture of "light orange" cadmium yellow with zinc white, as a water colour wash, faded in a month to one-fourth of its original intensity.

Cobalt Yellow (Aureolin).

This pigment is exclusively an artists' colour. It is usually prepared by rendering a solution of cobalt nitrate alkaline with caustic potash, diluting it with acetic acid, and treating it, whilst hot, with a concentrated solution of potassium nitrite. The crystalline precipitate which slowly forms is orange-yellow at first, then becomes brownish, and after being

washed is light golden yellow. It is a potassium cobalti-nitrite of the composition $[\text{Co}(\text{NO}_2)_6]\text{K}_3$, with varying amounts of water. According to Church, the pigment usually contains 3 mol., and under other conditions 4 mol. of water.¹ In the latter case it has a greenish tint. Church states that the anhydrous form is obtained by treating a solution of a cobalt salt acidified with acetic acid, with a concentrated solution of potassium nitrite, and keeping the mixture warm. The pigment is said to be obtained in an even more beautiful form when a current of nitric oxide, mixed with air, is passed into a solution of cobalt nitrate and potassium acetate, potassium carbonate being added from time to time (Rosenheim and Koppel).

According to R. H. Adie and T. B. Wood,² a particularly lustrous cobalt yellow is prepared by adding a solution of sodium cobalti-nitrite, acidified with acetic acid, to a dilute solution of potassium acetate or nitrate. The pigment obtained in this way possesses the composition:—



Church states that it is equal in value to the other varieties of aureolin. As a water colour it has the advantage of being much less soluble in water than the older pigments of this class, and of not sinking so deeply into the paper. By heating to 115° the water can be partially driven off. The slow drying of aureolins as oil colours and the dirty appearance which they assume, are due, as Church has pointed out, to the presence of water.

As regards fastness to light and compatibility of these pigments in mixtures with others, divergent opinions exist. According to Mierzinski and Zerr and Rübenkamp, cobalt yellow is unstable in the light. J. Bersch and Church describe it as permanent in water colour washes. According to experiments made by Church, its intensity diminished 10 per cent. within ten years. A. Eibner's experiments proved that as a water colour wash exposed to direct sunlight for six years it showed no change. According to Gentele, it is miscible with most other colours, even those containing sulphur. A. W. Keim observed instability in mixtures with several other pigments. These varying opinions can probably be traced to differences in the water-content of the individual varieties.

Fastness to Zinc White.—A 5 per cent. mixture of cobalt yellow with zinc white, exposed to light as a water colour wash, was only slightly changed after two months (late autumn).

¹ Cf. also, Rosenheim and Koppel, *Z. anorg. Chem.*, 1898, 17, 59.

² *J. Chem. Soc.*, 1900, 27, 1076.

Analysis.—Cobalt yellow is perceptibly soluble in water; it is only feebly attacked by alkali solutions and dilute acids, and is only slowly blackened by hydrogen sulphide. Ammonium sulphide decomposes it immediately. When heated it decomposes, giving off brown fumes of nitrogen peroxide, and leaves a black residue of cobalt oxide and potassium hydroxide, which has an alkaline reaction and dissolves in dilute acids forming a red solution.

The name *Jaune Indien* or *Indian yellow* which is sometimes given to cobalt yellow is a false "substance designation" intended to suggest its similarity with genuine Indian yellow (Puree). This similarity, however, does not exist either as regards colour tone, genuine Indian yellow having a brownish tint, or in those properties of technical importance in painting, since Indian yellow is a glazing colour, and cobalt yellow a body colour.

Nickel Yellow.

This pigment is obtained by treating nickel sulphate with sodium phosphate and calcining the resulting precipitate. According to Mierzinski and Zerr and Rübenkamp, the colour is very stable and of good covering power.

The Yellow Chromium Pigments.

Chrome Yellow.

(a) *Technically pure Varieties of Chrome Yellow.*—These are, essentially, neutral lead chromate, and vary in shade from pale to dark golden yellow. According to Zerr and Rübenkamp,¹ the shade of these commercial preparations depends upon the concentrations of the solutions of the reacting substances, their temperature, the way in which they are brought together, the period of reaction, and the manner in which the precipitated pigment is washed. The preparation is carried out with dilute solutions at the lowest possible temperature, the solutions being kept in constant motion during the precipitation. Loss of time must be avoided in the precipitation and in the washing process. K. Jablczynski² has pointed out that chrome yellow undergoes partial hydrolysis on washing, whereby a certain amount of chrome red is formed which causes subsequent darkening. It is stated that this phenomenon does not occur if the washing process is not exhaustive, or if an excess of at least 5 per cent. of lead acetate is used in the precipitation.³ According to Gnehm, this darkening does not take

¹ *Colour Manufacture*, p. 130.

² *Chem. Ind.*, 1908, 31, 731; *J. Soc. Chem. Ind.*, 1909, 28, 30; *Farben-Zeit.*, 1909, 14, 1041.

³ According to Zerr and Rübenkamp, $37\frac{1}{2}$ parts of bichromate to 100 parts of lead acetate.

place when lead nitrate is used instead of lead acetate, provided that a slight excess is employed.

(b) *Chrome Yellow Substratum Colours*.—The lemon-yellow shade of chrome yellow, for which there has been a demand since the introduction of zinc yellow, cannot be obtained by observing the above precautions, as these do not serve to prevent the increase of density of chrome yellow owing to increase in size of grain.¹ Double salts of lead chromate and lead sulphate (lead sulpho-chromates possessing the composition $\text{PbCrO}_4 \cdot \text{PbSO}_4$ and $\text{PbCrO}_4 \cdot 2\text{PbSO}_4$), varying in tint from sulphur-yellow to lemon-yellow, have been known for a considerable time.² The commercial brands of "lemon" chrome yellow are therefore prepared in such a way that, simultaneously with the precipitation of chrome yellow from very dilute solutions, a definite amount of lead sulphate in a very finely divided condition is produced, and this is taken up by the chrome yellow, forming the double salts, and thus preventing the production of more complex and more deeply coloured products. Jablczynski is of opinion that the durability of the lemon-yellow tone of this chrome yellow is due to the sparing solubility of lead sulphate in water being sufficient to prevent the hydrolysis of the pigment on washing.

(c) *Adjuncts to Chrome Yellow Colours*.—Since technically pure chrome yellow is too dear for various industrial purposes, adjuncts such as gypsum, heavy spar, China clay, whiting or white infusorial earth are added to it in order to reduce the cost. These inferior qualities are known as Baltimore chrome yellow, American or French chrome yellow, Imperial, King's, Canary, Cologne, Leipzig, New, Paris, Lemon-, Zwickau yellow, etc.

Chrome Orange and Chrome Red (Derby Red).

These pigments consist of basic chromate of lead, $\text{Pb}_2(\text{OH})_2\text{CrO}_4$, or of mixtures of this with neutral chrome yellow. They are prepared either by treating basic lead acetate with potassium or sodium bichromate, or by agitating lead sulpho-chromates with caustic soda in hot solution. The designations "Chrome Cinnabar," "Chrome Garnet," and "Chrome Ruby" are used for the deepest shades of chrome red.

That the shades of the chrome oranges and chrome reds depend on the size of grain is shown by the fact that these pigments do not stand fine grinding. They lose thereby in depth and richness, and assume pale to dark orange tones.

¹ Cf. H. Amsel, *Z. angew. Chem.*, 1896, 9, 613.

² M. Willenz, *Bull. Assoc. Belg. des Chim.*, 1898, 12, 163; *Fischer's Jahresber. f. Chem.*, 1898, p. 417.

Valuation of the Yellow and Red Chromium Colours and of the Raw Materials used in their Preparation.

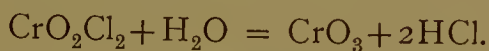
(a) **Examination of Potassium Chromate.**—This comprises the detection of potassium and aluminium sulphates, potassium nitrate and potassium chloride.

Potassium Sulphate.—The solution of chromate is boiled with excess of hydrochloric acid with addition of alcohol, and the green solution obtained then treated with barium chloride.

Aluminium Sulphate.—10-15 g. of chromate are dissolved in water, hydrochloric acid and alcohol added, and the solution boiled until uniformly green. The solution is then treated with an excess of potassium hydroxide, boiled, filtered, and the filtrate tested for alumina in the usual manner.

Potassium Nitrate.—10-20 g. of powdered potassium chromate are warmed in a retort with a mixture of equal quantities of concentrated sulphuric acid and water. The distillate is collected in a cooled receiver, and tested for nitric acid which decolorises a drop of dilute indigo solution on warming.

Potassium Chloride.—The presence of this salt is indicated in the preceding test by the formation of yellowish-red fumes of chromium oxychloride, which condense in the receiver to an orange-yellow liquid, chromic and hydrochloric acids being formed.



The hydrochloric acid so formed may, moreover, be detected in the distillate.

(b) **Examination of Chrome Yellow.**—The complete analysis, which is seldom necessary, is carried out in the usual manner by reducing a solution of the substance with hydrochloric acid and alcohol. The solution is then cooled and treated with strong alcohol, and the lead chloride which separates out collected on a tared filter paper, previously dried at 120°. The precipitate is washed with alcohol, dried at 120°, and weighed. The chromium contained in the filtrate is precipitated as hydroxide by ammonia, too great an excess of the reagent being avoided. The quantitative estimation of chromic acid can usually be satisfactorily carried out by Bunsen's chlorine method, which consists in boiling with hydrochloric acid, passing the chlorine evolved into a solution of potassium iodide, and titrating the liberated iodine with sodium thiosulphate.

The more important adulterants of chrome yellow are clay, heavy-spar, lead sulphate, gypsum, and chalk. These substances are determined qualitatively by Wittstein's method¹ as follows:—1 g. of

¹ *Dingl. polyt. J.*, 1873, 210, 280.

the sample is treated in a flask with 7 g. of pure hydrochloric acid of sp. gr. 1.12; effervescence indicates the presence of chalk. The mixture is heated until the remaining sediment is quite white and permanent, 1 g. of 90 per cent. alcohol is then added, and the heating continued until the colour of the solution is pure green. 100 c.c. of water are added, the solution filtered, and the precipitate washed until the washings no longer give reactions for free acid or sulphate. The residue on the filter paper may consist of heavy spar and clay, which can be separated by the usual methods. The filtrate is tested with barium chloride; if sulphates (lead sulphate and gypsum) are present 1 g. of sodium sulphate is added to the solution, which is stirred until the salt is dissolved, and then allowed to settle. A precipitate indicates the presence of lead sulphate; this is filtered off, the chromium in the filtrate precipitated with ammonia, and the second filtrate tested for calcium (gypsum).

Adulteration with lead sulphate can also be easily detected by Löwe's method¹ as follows:—The finely powdered chrome yellow (or chrome red) is shaken with a cold, moderately strong solution of sodium thio-sulphate, in which lead sulphate is readily soluble. Lead can be recognised in the filtrate by treating with neutral potassium chromate, and can be estimated quantitatively by precipitation from this solution with sulphuretted hydrogen. The lead sulphide thus obtained is washed, and converted in the usual manner into lead sulphate.

For the estimation of heavy spar, gypsum, chalk, barium carbonate and lead sulphate, H. Amsel² suggests the following method:—Half a gram of the sample is shaken with 10-15 c.c. of 10 per cent. potassium hydroxide solution in a beaker, and after addition of 10 c.c. of water the mixture is boiled for five to ten minutes over the free flame. All lead compounds, together with calcium sulphate, are thus dissolved, only barium sulphate and calcium carbonate, if present, remaining insoluble. Without filtering, the alkaline solution is then strongly acidified with concentrated hydrochloric or nitric acid; the alkaline plumbite is thereby converted into soluble lead chloride or lead nitrate, and any calcium carbonate present is dissolved. The solution is again boiled, and then filtered; the heavy spar remaining on the filter paper is well washed with hot water, dried, ignited, and weighed. By this method heavy spar is obtained quite free from lead chromate and other lead compounds, whereas in Wittstein's method the residue remaining after treatment with sodium carbonate contains lead chromate. The acid filtrate is neutralised with sodium carbonate, whereby lead and calcium are precipitated as carbonates, while sulphuric and chromic acids remain in solution as alkali salts; to ensure complete oxidation a little bromine

¹ *Polyt. Notizbl.*, 1873, p. 369.

² *Z. angew. Chem.*, 1896, 9, 613; *J. Soc. Chem. Ind.*, 1896, 15, 830.

water is added, and the solution heated on a gently boiling water-bath until it no longer smells of bromine. The insoluble carbonates are then filtered off from the solution of sodium chromate and sodium sulphate, and the chromium estimated as chromium oxide. For this purpose the solution is acidified with hydrochloric acid, evaporated to dryness in a porcelain dish to completely remove any remaining traces of bromine, the residue dissolved in about 30 c.c. of water, a few drops of hydrochloric acid added, and finally 5 c.c. of alcohol, whereby the chromate is reduced to a chromic salt. A portion of the bromine is retained by the excess of sodium carbonate and is only set free again after acidifying; it is, therefore, absolutely necessary to evaporate to dryness before proceeding with the reduction. After reduction is complete—that is, when the liquid no longer smells of alcohol—excess of ammonia is added, and the solution warmed for ten to fifteen minutes on the water-bath; as a rule it is advisable to add a further quantity of water, for during the process of reduction the necessarily prolonged heating may render the solution too concentrated. The precipitate, which does not come down immediately, is filtered off, washed well with hot water, dried, ignited in a porcelain crucible, and weighed. From the weight of Cr_2O_3 obtained, the value for CrO_3 may be calculated.

The ammoniacal filtrate is acidified with hydrochloric acid, and the sulphuric acid, if present, estimated as barium sulphate in the usual manner.

The carbonates of calcium and lead, and possibly lead peroxide remaining on the filter paper, are treated with hydrochloric acid in which they dissolve with evolution of chlorine; lead and calcium are then determined by the ordinary analytical methods. The precipitation of lead with sulphuretted hydrogen must be carried out either in dilute hydrochloric acid solution, or preferably in acetic acid solution, as otherwise it may easily happen that all the lead is not precipitated; it is also advisable to weigh the lead as sulphate and not as sulphide. In this way zinc may also be tested for in the filtrate from the lead sulphate, as it is likewise precipitated by sulphuretted hydrogen, in acetic acid solution. The precipitation with sulphuretted hydrogen may be entirely avoided, provided the solution does not contain zinc as well as calcium and sufficient bromine has been added to convert all the lead carbonate into lead peroxide. In this case the black residue consisting of lead peroxide and calcium carbonate is treated with dilute nitric acid in which calcium carbonate is readily soluble, while lead peroxide is quite insoluble. The latter is then estimated as lead sulphate, by dissolving in hydrochloric acid and evaporating the solution with sulphuric acid. The lead may also be determined volumetrically by placing the filter paper containing the peroxide in a porcelain dish, treating it with about 10 c.c. of dilute nitric acid, adding

20 c.c. of $N/5$ oxalic acid, and heating the solution to boiling; the excess of oxalic acid is titrated back with $N/5$ permanganate solution. 1 c.c. $N/5$ oxalic acid = 20.71 mg. lead, or 22.29 mg. lead oxide.

The complete analysis of chromium colours, by the method of M. Willenz,¹ is carried out as follows:—1 g. of the finely powdered material is treated, with gentle heating, with 100 c.c. of dilute hydrochloric acid (1:20), the clear solution filtered off, as much of the insoluble residue as possible being retained in the beaker; the main bulk of the residue, as well as the small portion on the filter paper, is washed with warm water. Calcium and sulphuric acid are estimated in the filtrate, which contains the calcium originally present as carbonate, and calcium sulphate. The residue is digested at the ordinary temperature with 50 c.c. of ammonium acetate solution (sp. gr. 1.04) which should be neutral or slightly alkaline. The solution is then decanted off, and the residue washed with warm water as before; lead sulphate goes into solution and is estimated by evaporating the solution to dryness in a weighed platinum dish. After driving off ammonia and acetic acid, the residue is ignited with sulphuric acid. The residue insoluble on treatment with ammonium acetate may contain lead chromate, barium sulphate, and alumina. It is suspended in 50 c.c. of water, 25 c.c. of potassium hydroxide solution (112 g. per litre) added, and the mixture boiled for about ten minutes; alumina and barium sulphate remain unchanged and can be separated by the usual methods: lead chromate dissolves, forming potassium chromate and potassium plumbate.

(c) Examination of Chrome Orange and Chrome Red.—In this case, besides the examination similar to that of chrome yellow, an estimation of basic lead oxide is also necessary. For this estimation a finely powdered portion of the colour is treated with acetic acid, whereby basic lead oxide is alone dissolved. The neutral lead chromate, which remains insoluble, is dried and weighed, and the amount of basic lead oxide estimated by difference.

Fastness to Light.—The chrome yellows are far less fast to light than zinc yellow, baryta yellow, and strontium yellow. The most unstable, with few exceptions, are the lemon-coloured and pale golden yellow varieties, whereas the chrome oranges are considerably more permanent in light. The chrome reds are more sensitive to light than the best chrome oranges. Within seven months very distinct to extremely marked changes have been observed. Some chrome oranges withstand exposure to light for fourteen months without showing much darkening. The palest varieties assume a dirty green appearance; the chrome oranges become greenish-yellow with a brownish tint, and the chrome reds blacken like the cinnabars. The action of light in the case of many lemon-yellow varieties is distinctly noticeable after only four to five

¹ *Bull. Assoc. Belg. des Chim.*, 1898, 12, 163; *J. Soc. Chem. Ind.*, 1898, 17, 953.

days. Oil vehicles form no protection against the action of light on chrome yellows. Church regards the action of light as causing a reduction to green chromic oxide.¹ According to Eder,² the brown chromium superoxide or dioxide, $\text{CrO}_2 \cdot \text{Cr}_2\text{O}_4$, or $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$, is formed.

Behaviour in Mixtures (Fastness to Zinc White).—The change which mixtures of cadmium yellow with chrome yellow undergo has already been mentioned. Mixtures of cobalt greens and chrome yellow change colour after a year, becoming brownish-green. In both instances the change is probably due to a partial reduction of the chromate. All chrome yellow pigments are incompatible with lime, since they become converted into basic chromates. The accelerating influence of zinc white on the lack of permanence of pigments in the light is particularly noticeable in the case of the chrome yellows. 50 per cent. mixtures of zinc white with chrome lemon-yellow and chrome golden-yellow of known fastness to light, were rendered more intensely brown in fifteen days (autumn) than the same pigments without zinc white in seven months. The sensitiveness of chrome yellow towards hydrogen sulphide is well known. Since, at the same time, the chromic acid radical is also partially reduced, the discoloration cannot be completely removed by exposure to light. The chrome yellows are more stable towards sulphur dioxide than the zinc yellows.

Zinc Yellows.

(Zinc Chrome ; Lemon-Yellow.)

Zinc yellow, unlike chrome yellow, cannot be obtained in different shades, as zinc does not possess the property of forming differently coloured basic chromates. On the other hand, the tone of zinc yellow is a very pure, delicate but fiery yellow, free from any reddish tint. In consequence, it forms mixed tones of purer green than chrome yellow, and is chiefly used for the production of *Zinc greens* (green cinnabars). It is now prepared exclusively from zinc white, only the best qualities of the latter, the so-called "snow white" or zinc white "green seal," being used. According to Murdoch (1847), the zinc white is treated with a definite quantity of concentrated sulphuric acid, and partially converted into zinc sulphate; a solution containing the calculated amount of potassium bichromate is then added. The zinc yellow obtained in this way is not pure zinc chromate, but the double salt $3(\text{ZnCrO}_4) \cdot \text{K}_2\text{Cr}_2\text{O}_7$, precipitated on the unchanged zinc oxide. It is, therefore, a substratum pigment.

Zinc yellow is not quite insoluble in water, as the double salt is slightly decomposed with the liberation of free potassium chromate.

¹ *The Chemistry of Paints and Painting*, p. 162.

² *Photochemie*, p. 175.

Fastness to Light and Air.—Zinc yellow is to a marked degree more stable to light than the chrome yellows. Water colour washes exposed to direct sunlight for five years remained unchanged. It is more stable than chrome yellow towards hydrogen sulphide, because the zinc present undergoes no change, and it also appears to be less affected by the reducing action of the gas. On the other hand, like barium yellow and strontium yellow it is more rapidly attacked by sulphur dioxide than is chrome yellow.¹

Barium Yellow.

(Yellow Ultramarine; Lemon-Yellow; Permanent Yellow.)

This colour consists of barium chromate. It possesses a much weaker tone than zinc yellow, but its stability in light appears to be greater. Water colour washes showed no change of tone in five and a half years. Towards sulphur dioxide, however, like zinc yellow and strontium yellow, it is more sensitive than the chrome yellows. As a pigment it is of little or no value, its more important application being in the manufacture of matches, where it partly replaces potassium bichromate in making the igniting composition.

Strontium Yellow.

(Yellow Ultramarine.)

This pigment is strontium chromate. Its shade is more fiery than that of barium yellow. As regards stability to light and behaviour in other respects, it is similar to the latter.

A chromate of calcium is sold under the names of *Steinbühl Yellow*, *Gelbin*, *Yellow Ultramarine*, but barium yellow also frequently passes under these names.

Compatibility in Mixtures (Fastness to Zinc White).—All the yellow chrome colours mentioned, including zinc yellow, are incompatible with white lead as they react with it to form basic chromates, and the tone of the mixture, therefore, becomes reddish after a time. Moreover their instability as chromates comes into play in mixtures with zinc white, Naples yellow, cobalt blue, *cœruleum*, ultramarine, and cobalt green. The reactions which take place in these cases are not yet satisfactorily explained.

Zinc yellow, strontium yellow, and barium yellow, when made up with zinc white into pale-coloured mixtures and used as water colours, are also unstable in direct sunlight. 1 per cent. mixtures of these pigments faded very considerably in two months (October to December).

¹ Zerr and Rübencamp, *Colour Manufacture*, p. 129, state that it is unaffected by sulphurous gases.

V. RED PIGMENTS.

(a) Naturally occurring Red Pigments.

Red Ochres and other Red Mineral Colours.

These colours are essentially naturally burnt ochres containing varying quantities of iron. They have been known and used from the earliest times under such names as *Rubrica*, *Sinopis*, *Armenian bole*, *Lemnos earth*, etc., and occur chiefly in volcanic districts. Their application at the present day is more limited than that of the artificial red iron colours. Deposits are found in Italy (Treviso, Pozzuoli), France, England, Bohemia, the Harz Mountains, Hesse-Nassau, near Saalfeld, etc. This class includes Raddle (red chalk) or red bole, crude red iron-stone, and micaceous iron. The two last-named materials require to be submitted to calcination, etc., before they can be used for the preparation of paints.

Red Bole occurs in Armenia, also in Lemnos, Malta, Hungary, Saxony, Silesia, near Wunsiedel, etc., and is a fairly pure clay coloured by ferric oxide. The burnt product comes on to the market as *Stone red*, etc., and was used in the seventeenth and eighteenth centuries as a basis for pastel painting.

Pozzuoli Earth is a volcanic red earth found at Pozzuoli in the neighbourhood of Naples. In the purest form it is almost white or yellowish, but it may possess a reddish to flesh-pink colour owing to the presence of iron. It differs from the ochres and forms a kind of natural cement (Travertine) consisting of partly decomposed clay. It is decomposed by hydrochloric acid, and unlike the ordinary red clays it contains, besides alumina, lime, magnesia and potassium and sodium as essential components. In this respect it differs from the imitation Pozzuoli earths, which are frequently prepared on account of the comparatively high price of the genuine substance, and which are mixtures of English red, etc., and chalk. Genuine Pozzuoli earth, unlike these products, does not effervesce on treatment with acids.

(b) Artificial Products.

Commercial Names. — Berlin red, blood-red, brown-red, caput mortuum, chemical red, pale, dark and violet oxide of iron, iron saffron, angel red, English red, Indian red, Imperial red, Nuremberg red, Persian red, rouge, Pompeian red, Prague red, Prussian red, red oxide, scarlet-red, Venetian red.

All these substances contain ferric oxide as the chief constituent, and varying quantities of natural argillaceous components. Iron colours prepared from pyrites cinder and sludge mostly contain copper. The chief raw materials are red iron ore, hæmatite, iron ochre, bog iron ore and limonite. Besides these there are certain artificial and waste

products such as copperas, pyrites cinder, alum sludge and the vitriol sludge obtained in the manufacture of copper sulphate.

Red Oxide, which serves as a substitute for red lead, is prepared from the foregoing iron ores by calcining them in a reverberatory furnace. By this process the denser ores become porous and the earthy ores are rendered denser and more brittle. Red oxide contains from 82-88 per cent. of ferric oxide, and is a fine brownish- to bluish-red powder possessed of very considerable covering power and the greatest resistance to climatic influences. As an oil colour it protects iron objects effectively against rust. It is free from sulphuric acid, cheaper than red lead, and non-poisonous. The varieties prepared from pyrites cinder may contain sulphur.

The value of red oxide depends on the amount of ferric oxide it contains, and also on the temperature at which it has been roasted. As the latter rises, the amount of ferric oxide increases, without its solubility in hydrochloric acid becoming less; at the same time the specific gravity increases. If heavy adulterants, which can be easily recognised by qualitative analysis, are absent, the specific gravity thus provides a means of estimating the temperature of roasting. Keeping in view chemical properties and cost, a material of sp. gr. 4.2 would best meet practical requirements. Ability to withstand the action of acids and weather increases with an increase in specific gravity, and is determined by a boiling test with dilute acids. Reduction of the substance to a finer state of division increases its covering power, but does not lessen its stability towards acids. The latter is entirely dependent on the degree of heat employed in the manufacture.¹

English Red.

(Prussian Red; Venetian Red; Italian Red; Rouge; Colcothar.)

Under these designations red ferric oxide colours, varying in tone from pale yellowish-red to bluish-red, come into the market. They are prepared chiefly from alum or vitriol sludge. Their principal industrial application is as lime and cement colours, but they are also manufactured as artists' colours. As they frequently contain sulphates, they are, on this account, less suitable than red oxide for painting on iron. Owing to its extraordinary colouring power, English red is frequently "let down" with comparatively large amounts of adjuncts, chiefly gypsum (up to 80 per cent.). Gypsum may be already present, however, in the raw materials, or it may be formed during the roasting process from any chalk which is present. If the added gypsum has been previously burnt, the English red, when used as a water colour, becomes lumpy and thickens.

¹ Cf. H. Baucke, *Z. anal. Chem.*, 1898, 37, 668; *J. Soc. Chem. Ind.*, 1899, 18, 52.

An unadulterated English red possessed the following composition :—

	Per cent.
Water	4.35
Silica	11.35
Lime	3.0
Ferric oxide	78.4
Alumina	2.3
SO ₃	0.60
	<hr/> 100.00

It is well known that English red, in a similar manner to zinc white, affects the fastness to light of a series of organic colours such as indigo (Church) and especially the coal-tar pigments.

Caput Mortuum.—The oldest method of manufacturing this substance is by the calcination of ferrous sulphate. Nordhausen (fuming) sulphuric acid is obtained as the main product of the process. At a later period the Pilsen vitriol schists were used for this purpose. The residue obtained after calcination was formerly ground, and offered for sale without undergoing further treatment. At the present day it forms the raw material for the manufacture of valuable colours possessing various shades, which are prepared by grinding it with increasing amounts of common salt, and heating again up to definite temperatures in reverberatory furnaces. The duration of this calcining process plays an important part. Yellowish-red shades are obtained with 2 per cent., brownish with 4 per cent., and violet with 6 per cent. of salt.

According to B. Wöhler and Condrea the colour of the different kinds of caput mortuum is also dependent on the size of grain, and can therefore be altered by reduction of the latter.

All the red artificial iron colours are characterised by great colouring and covering power. In the case of those varieties which are used as grinding and polishing media (polishing rouge), hardness, together with fineness of grain, is of the greatest importance.

Velvet Red is a reddish-brown powder consisting of ferric oxide coloured by a mixture of "spirit-soluble" rosaniline blue and fuchsine.¹

Up to a comparatively recent period English red and caput mortuum colours were frequently "improved" by means of coal-tar dyes. These are detected by placing a portion of the colour on filter paper and moistening it with water, alcohol, or a mixture of alcohol and acetic acid, or by boiling with this mixture and filtering.

Analysis.—The estimation of moisture in ferric oxide colours is carried out by drying the colours at 110° until the weight is constant. Further loss on ignition is calculated as water of hydration, provided

¹ *Dingl. polyt. J.*, 1898, 308, 155.

that no sulphates are present. In the case of many iron colours there are difficulties in obtaining a solution in acids. They become more difficultly soluble the more strongly they are ignited, and the more silica they contain. For the purpose of estimating the contained iron it is best to fuse them with sodium carbonate. The pale varieties of English red dissolve on continued boiling in concentrated hydrochloric acid or aqua regia. Accessory components to be considered are manganese, alumina, magnesium, calcium, and silica.

Small quantities of gypsum, if present, are estimated by determining the amount of sulphuric acid in the acid solution after separation of the iron, aluminium, and manganese. If larger quantities are present the substance is extracted with a hot solution of sodium carbonate, and the amount of sulphate in the extract is determined. The estimation of basic ferric sulphates, which may be present in colours prepared from pyrites cinder and containing gypsum as well, cannot be carried out by this method.

In the examination of polishing rouge by A. Munkert's method,¹ 2 g. of the substance are boiled for some time with concentrated hydrochloric acid until the oxide of iron is completely dissolved; the solution is evaporated to dryness, the residue taken up with acid, and the solution filtered off from insoluble mineral matter. The filtrate is made up to 250 c.c. and 50 c.c. are used for estimating the sulphuric acid, after precipitation of the iron with ammonia. In a further 50 c.c., iron, aluminium, calcium, and magnesium are determined. Copper is estimated by decomposing 10 g. of the substance with concentrated hydrochloric acid, filtering off the insoluble residue, and reducing the ferric chloride solution with sodium hypophosphite in presence of excess of acid; the copper is then precipitated by sulphuretted hydrogen, and determined electrolytically.

The microscopic examination of the residue insoluble in acid (any soluble silica present can be removed by sodium carbonate solution) affords valuable evidence as to the nature and condition of the mineral admixtures, and frequently as to the method of manufacture.

Fastness to Light.—Artificial ferric oxide colours, provided that they are not "improved" with coal-tar dyes, are quite fast to light and are fully miscible with other colours. On the other hand, all these colours, like the burnt ochres, sienna earths, and umbers, possess the property of being slightly soluble in the usual fatty oils, and this solubility forms one of the causes of the subsequent darkening which they undergo when used as oil paints. English red has been stated to have an injurious effect on coal-tar colours on exposure of the pigments to light, as in the case of zinc white.

¹ *Z. angew. Chem.*, 1900, **13**, 593; *J. Soc. Chem. Ind.*, 1900, **19**, 672.

Red Lead (Minium).

Red lead is prepared on a manufacturing scale (*a*) by calcining lead oxide (PbO) in the form of massicot (not litharge¹) in muffle furnaces into which air is admitted. The commercial product obtained in this way is known under the name of "Crystal minium" or "true red lead." (*b*) By calcining powdered white lead. The red lead obtained by this process is of finer grain, warmer in tone and dearer than crystal minium, and is called "Orange lead." It also possesses greater covering power than the other brand. Crystal red lead is chiefly used as an oil colour, as a priming in painting on iron, as a packing material for joints in machinery, and for the preparation of red lead putty. The finer orange lead serves chiefly as a pigment, and when used as an artists' colour it is known as "Saturn red." (*c*) In this method lead sulphate is mixed with sodium carbonate and sodium nitrate and the mixture heated to a dull red heat. The reaction which takes place results in the formation of lead carbonate and lead oxide, and the latter becomes oxidised. This method of preparation is now very little used.

Red lead possesses the composition $\text{Pb}_3\text{O}_4[2(\text{PbO}).\text{PbO}_2]$.

Copper, bismuth, iron, and antimony have an injurious effect on the colour of red lead.²

An account of the preparation, properties, and decomposition of red lead has been published by J. Milbauer.³

According to Bolley-Stahlschmidt,⁴ litharge is impure lead oxide while massicot is the almost pure substance. Zerr and Rübencamp consider that the differences between the two substances lie in their physical condition. Litharge is to be looked upon as fused crystalline lead oxide. Owing to its density it can only be further oxidised with great difficulty; hence it is not suitable for the manufacture of red lead. On the other hand, massicot, which exists as a very delicate pale yellow powder, is very readily oxidised in the air. Both products should dissolve completely in nitric acid, and all the lead should be precipitated out of the solution by sulphuric acid, so that, on complete evaporation of the liquid remaining after filtration from the precipitate, only a minute residue should remain. The presence of calcium salts may be detected by dissolving in dilute nitric acid, excess being avoided; the solution is then diluted with water, and sulphuretted hydrogen passed in until it smells strongly of the latter. The precipitate is filtered off, and the filtrate treated with ammonia and ammonium oxalate. Evolution of

¹ Cf. Zerr and Rübencamp, *Colour Manufacture*, p. 259.

² O. Herting, *Chem. Zeit.* 1903, 27, 923; *J. Soc. Chem. Ind.*, 1903, 22, 1138.

³ "Physikalische, chemische und technische Studien über die Mennige"; *Chem. Zeit.*, 1909, 33, 513, 522, 950, 960; 1910, 34, 138, 1341; *J. Soc. Chem. Ind.*, 1909, 28, 612, 1049; 1910, 29, 282; 1911, 30, 37.

⁴ *Handbuch der chem. techn. Untersuchungen*, 6th ed., p. 355.

carbon dioxide, on addition of acid, indicates the presence of calcium carbonate or lead carbonate, only the latter being present if no calcium salts have been found by the previous test. Carbon dioxide is estimated in an ordinary Schrötter or similar apparatus. Particles of earth, brick dust, ruddle and red ochre are either insoluble in nitric acid or are found in the solution after precipitation of the lead by sulphuric acid; the same holds good for ferric oxide, which is often present in litharge. Stannic oxide remains in the residue insoluble in nitric acid, but is seldom contained in any considerable quantity in litharge. Copper is detected by digesting a small portion of the sample with ammonia, a blue coloration being obtained when the metal is present to any considerable extent. Litharge and red lead, when used in the manufacture of glass, must be quite free from copper and ferric oxides.¹ According to T. Salzer,² nitrous acid and gypsum are occasionally found in litharge.

The Analysis of Red Lead. A. Examination for Impurities.—Red lead becomes dark violet to black when heated; on cooling it returns to its original hue. It is soluble in glacial acetic acid, and in a mixture of nitric acid with either oxalic acid or sugar solution, with evolution of carbon dioxide. According to F. P. Dunnington,³ perhydrol is now used for adding to the nitric acid in dissolving red lead. A. Partheil⁴ has suggested the use of lactic acid for this purpose, as when oxalic acid is employed insoluble lead oxalate may be formed. The use of this reagent, however, has also been given up, and hydrogen peroxide is universally employed. Adulterants such as brick dust, ferric oxide, heavy spar, etc., which remain undissolved, are thus detected. According to L. Opificius,⁵ red lead is also soluble in nitric acid of sp. gr. 1.2 containing metallic copper. Dilute nitric acid and aqueous acetic acid form lead salts, and at the same time lead peroxide separates out. Dilute hydrochloric acid acts similarly. With excess of concentrated hydrochloric acid, lead chloride is formed and chlorine evolved. Concentrated sulphuric acid decomposes red lead with evolution of oxygen and formation of lead sulphate. Sodium hydroxide has no action.

R. Frühling⁶ states that the insoluble residue, after treating red lead with dilute nitric acid and sugar solution or hydrogen peroxide, should not amount to more than 1 per cent. if the red lead is to be used for pharmaceutical purposes—*e.g.* for plasters. On the other hand, as much as 10 per cent. is permissible when it is employed in the preparation of oil colours, metal paints, joints in steam pipes, etc.

¹ Cf. the section on "Glass," Vol. I., p. 628.

² *Pharm. Zentr.*, 1889, 29, 645; *Z. anal. Chem.*, 1889, 28, 734.

³ *Z. anal. Chem.*, 1889, 28, 338.

⁴ *Chem. Zeit.*, 1907, 31, 941.

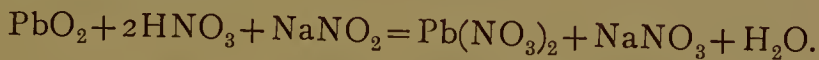
⁵ *Ibid.*, 1888, 12, 477.

⁶ *Z. angew. Chem.*, 1889, 2, 68.

J. F. Sacher¹ uses formaldehyde instead of hydrogen peroxide for the purpose of obtaining a solution of red lead in nitric acid, whilst P. Beck,² like Dunnington, recommends the use of 30 per cent. hydrogen peroxide. This method can also be used in the estimation of the insoluble residue in red lead that has been "let down" with barium sulphate.

B. *Estimation of the Content of Lead Peroxide.* (a) *Volumetric Methods.*—According to P. Beck, the volumetric method of A. Lux,³ which depends on the use of *N*/5 oxalic acid and permanganate, and was formerly employed for this purpose, gives less accurate results than the iodometric method of G. Topf and W. Diehl.⁴ P. Beck⁵ has described a variation of this method, making use of carbon dioxide. An alternative volumetric method is that of M. Liebig, jun.,⁶ according to which 0.5 g. of the sample is treated in a small Erlenmeyer flask with 25 c.c. of *N*/10 sodium thiosulphate and 10 c.c. of about 30 per cent. acetic acid, and dissolved by shaking; 10 c.c. of potassium iodide solution (1:10) and 2-3 c.c. of zinc iodide starch solution are then added, and the solution titrated with *N*/10 iodine solution. The number of cubic centimetres of iodine solution required, multiplied by 239.1, gives the percentage of PbO₂ in the red lead. The end of the reaction is sharply indicated by the lemon-yellow colour of lead iodide changing to a dirty dark yellow.

E. Szlerkhers⁷ uses sodium nitrite, which reacts with PbO₂ according to the following equation:—



5 g. of red lead are warmed for a quarter of an hour with 100 c.c. of boiling water and 5-7 c.c. of pure nitric acid on the water-bath; the solution is allowed to cool down to 50°, treated, drop by drop, with excess of standardised sodium nitrite solution (about 1 per cent.), and the excess of nitrite titrated back with permanganate solution (0.8 per cent.).

In the course of a critical examination of the various methods, A. Chwala and H. Colle⁸ recommend the following procedure:—1-2 g. of the sample are treated with 100 c.c. of cold *N*/1 nitric acid and 25 c.c. of *N*/1 oxalic acid. The mixture is heated until decomposition is complete, which requires ten to fifteen minutes. The solution is then titrated, at a temperature of 70°-80°, with *N*/1 or *N*/5 permanganate, allowing the main bulk to run in rapidly, and then continuing the titration rapidly to the end-point.

(b) *Gravimetric Method.*—For the gravimetric estimation H.

¹ *Chem. Zeit.*, 1908, 32, 62; *J. Soc. Chem. Ind.*, 1908, 27, 169.

² *Z. anal. Chem.*, 1908, 47, 465.

³ *Ibid.*, 1880, 19, 153.

⁴ *Ibid.*, 1887, 26, 296.

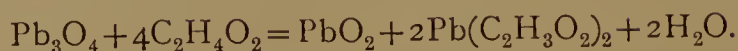
⁵ *Loc. cit.*

⁶ *Z. angew. Chem.*, 1901, 14, 828; *J. Soc. Chem. Ind.*, 1901, 20, 1027.

⁷ *Ann. Chim. anal.*, 1902, 7, 214; *J. Soc. Chem. Ind.*, 1902, 21, 1156.

⁸ *Z. anal. Chem.*, 1911, 50, 209; *J. Soc. Chem. Ind.*, 1911, 30, 802.

Forestier¹ suggests the use of acetic acid, which reacts in accordance with the equation :—



1 g. of red lead is heated for half an hour with 10 c.c. of 10 per cent. acetic acid and 20 c.c. of distilled water on the water-bath, and the lead peroxide which separates out is estimated either by direct weighing or by titration.

J. F. Tocher² recommends the following modification of a method given by Sutton for estimating the amount of peroxide in red lead: 2.064 g. of red lead are treated with 50 c.c. of *N*/1 nitric acid (sp. gr. 1.05) in the cold; PbO dissolves and PbO₂ remains insoluble. If the solution be then heated almost to boiling and 50 c.c. of *N*/5 oxalic acid added, the PbO₂ is nearly all dissolved; the solution is then treated with dilute sulphuric acid and titrated with *N*/5 permanganate until the red coloration is permanent. The number of cubic centimetres of permanganate required, subtracted from 50, gives the percentage of peroxide in the red lead.

Tocher also recommends a method in which red lead is treated with nitric acid of sp. gr. 1.2, then with barium hydroxide, sodium sulphate, sulphuric acid, oxalic acid and permanganate.

The better qualities of red lead, when ignited in a covered crucible, lose from 2.4-2.6 per cent. of oxygen; inferior qualities lose less down to as little as 1.3 per cent.

The amount of lead peroxide contained in the commercial varieties of red lead varies from 26.32-34.89 per cent.

Fastness to Light.—Red lead, especially in the form of powder, is not faster to light than vermilion; it becomes black owing to oxidation to lead peroxide. As an oil colour it is much more stable.

Behaviour in Mixtures (Fastness to Zinc White).—Red lead is incompatible with copper pigments such as verdigris, and this is also the case with the arsenic greens—Schweinfurth green, Scheele's green etc. In these cases formation of lead peroxide probably takes place. Eight per cent. mixtures of red lead with zinc white as water colours, when exposed to direct sunlight under glass, faded considerably within a month (November).

Of all mineral pigments red lead has the greatest effect on the period of drying occupied by the fatty drying oils (formation of lead soap). In combination with the oils it forms pastes which rapidly harden and are used, as already mentioned, as packing for making close joints in ironwork, etc. The serviceability of red lead as a basis for painting on iron has recently been questioned. According to Toch, it promotes

¹ *Z. angew. Chem.*, 1898, 11, 176.

² *Pharm. J.*, 1900, 64, 310; *J. Soc. Chem. Ind.*, 1900, 19, 471.

the rusting of iron by direct oxidation; red lead, however, is one of the oxides of lead which take up oxygen. Whether the formation of lead soap and the hydrolysis of the latter cause considerable quantities of moisture to collect locally, and thus set up rusting of the iron, is questionable. In view of the fact that, at the present day, it is almost universally accepted that lead soaps do not admit of hydrolysis to any considerable extent, the above assumption does not appear to be sufficiently well founded. According to Janoin, the electric currents set up in coats of red lead paint on ships immersed in sea water, and due to the presence of sodium chloride, give rise to corrosion of the ships' bottoms.

Artificially coloured Varieties of Red Lead.—At one time certain productions were frequently found on the market as cinnabar substitutes, the particular hue they possessed being obtained artificially by colouring red lead with eosin or azo-dyes, or by precipitation of the latter on to the mineral colour. These products have now been almost entirely superseded by the far superior cinnabar substitutes produced from coal-tar dyes which are fast to water and to oil. (Newer Signal reds.) Amongst the older productions of this nature having red lead as a base are the following:—

“*Carminette Yellow*”¹ is a heavy, warm, red powder which, on heating with distilled water, forms a pink solution, having a beautiful green fluorescence. The greater portion remains insoluble in water, and consists of red lead which is coloured by “eosin extra yellowish.”

“*Carminette Blue*” is a similar product, but a shade darker, and consists of red lead coloured with a bluish eosin.

The products known as “*Carminette blue-red*, reddish-yellow, warm-red and warm-dark,” are similarly constituted.

“*Cinnabar Imitation*,” or “bluish and yellowish cinnabar substitute,” consists likewise of red lead coloured with Rose Bengal or a mixture of this dye with some cochineal scarlet 2R.

Garnet Red,² a heavy, warm-red powder, is red lead coloured with crocein, while another quality consists of orange lead coloured with Ponceau 2R and 3R.

These pigments become brown on treatment with dilute nitric acid, and in this way the presence of red lead can be recognised.

Brilliant Scarlet.

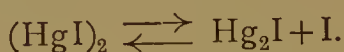
(Iodine Red; Mercury Iodide; Scarlet-Red.)

This pigment, which is only used as an artists' colour, is mercuric iodide. It occurs in nature as the mineral coccinite. Brilliant scarlet

¹ M. Bottler, *Dingl. polyt. J.*, 1898, 308, 153.

² Cf. M. Bottler, *Dingl. polyt. J.*, 1898, 308, 153.

is one of the most unreliable of mineral pigments. It is dimorphous. The red modification is the stable form at ordinary temperatures, and crystallises in the quadratic system. When heated, it passes into the yellow rhombic form. Both forms are enantiotropic, that is, mutually convertible into one another. The yellow modification seldom changes of its own accord, but passes into the red form when subjected to rubbing, pressing, or on heating below 120° ; according to W. Schwarz, the transition temperature of the two forms is $126^{\circ}.3$. The formation of the red form from the yellow takes place with evolution of heat. When exposed to light it also becomes yellow. When mixed with zinc white it turns blackish-violet even in twenty-four hours (November), and passes later into the yellow modification. The first change is a light reaction which is reversible, and may be looked upon as taking place according to the equation:—



When brought into contact with metallic iron, mercuric iodide undergoes decomposition with the formation of mercury and ferrous iodide. Brilliant scarlet is recognised by the colour change on heating. Its degree of purity is indicated by a sublimation test, or by dissolving it in potassium iodide.

Vermilion (Cinnabar).

This pigment is mercuric sulphide, HgS . It occurs native as cinnabar, but this form is only sold on a very small scale at the present day, for in beauty of shade it is inferior to the manufactured varieties, and particularly to those prepared by the wet method. The principal methods of manufacture are the dry method, in which black mercuric sulphide is first formed, and is then converted into the red modification by sublimation; and the wet method, in which at least one of the materials, such as potassium pentasulphide, is used in a dissolved condition.¹ The manufactured products are usually sold as "pale" and "dark" according to their shades. "Carmine cinnabars" are prepared in the wet way. The statement which is frequently made, that these pigments contain English red, is incorrect. The manufacturer's specifications are expressed either by figures or by letters. Under the designation "Chinese vermilion" some particularly warm vermilions of superior fastness to light are sold.

Analysis.—Metallic mercury, free sulphur and iron are best detected by dissolving the vermilion in potassium monosulphide solution (1:1). Brunner observed that the pigment dissolved in this solution with extraordinary ease. When the ferrous sulphide has settled, the solution is colourless. If metallic mercury is present, it settles after some time

¹ Cf. Zerr and Rübenkamp, *Colour Manufacture*, p. 274.

at the bottom of the vessel as a grey cloud. The presence of free sulphur is detected by the yellow coloration of the solution, which, however, disappears in time as the sulphur slowly combines with the potassium monosulphide. Sulphur may also be detected in the usual way, either by digesting with potassium hydroxide or by extracting with carbon bisulphide, provided that the sulphur is present in the crystalline state.

The quantitative determination is carried out by extracting with sodium carbonate solution, and then oxidising to sulphate. In order to ascertain the presence of foreign adjuncts such as heavy spar, clay, red lead, chrome red, brick dust, English red, etc., which, however, are very seldom present to-day, the sublimation method was formerly used. In testing qualitatively for these impurities or intentional additions, the use of potassium monosulphide is preferable. After filtration the residue must not be washed with water at first, but with dilute potassium hydroxide solution, as otherwise Brunner's salt ($\text{HgS} \cdot \text{K}_2\text{S} \cdot 5\text{H}_2\text{O}$), which has been formed, will be decomposed with separation of black mercuric sulphide. Dragon's blood and coal-tar dyes are detected by extracting the sample with alcohol; "carmined" vermilion is recognised by spotting a portion with ammonia on filter paper. These adjuncts, however, are very seldom present nowadays. On the other hand, so-called "Secondary Vermilion" is manufactured, which consists of vermilion intimately mixed with heavy spar. Sulphide of arsenic is recognised by boiling with sodium hydroxide, acidifying with hydrochloric acid, and passing in sulphuretted hydrogen. Combined sulphur is estimated, according to P. Jannasch and H. Lehnert,¹ by burning the vermilion in a current of oxygen and collecting the volatile products in hydrogen peroxide. The mercury which comes over is dissolved by adding aqua regia, the solution evaporated to dryness, the residue taken up with water and hydrochloric acid, and the sulphate formed precipitated with barium chloride.

Hue and Fastness to Light.—Vermilions prepared in the wet way exhibit a much greater variety of shade than those manufactured by the sublimation process, and also differ from the latter in possessing greater brilliance. By the wet method colours ranging from bright warm orange to dark dull blue-red are obtained. Both a light and a dark variety are nearly always obtained together as the products of one single process of preparation; they can be separated by levigation. These differences of colour depend on size of grain, as in the case of the oxides of mercury, oxides of iron, etc.

According to Church² and A. W. Keim,³ the palest artificial

¹ *Z. anorg. Chem.*, 1896, 12, 129.

² *The Chemistry of Paints and Painting*, p. 168.

³ *Techn. Mitt. f. Malerei*, 1907, 23, 212.

vermilions are the most unstable to light. A. Eibner observed, on the contrary, in one hundred and eight individual tests, that, of the vermilions manufactured in the wet way, the darker bluish-tinged and medium shades darkened much more intensely than the palest varieties within the same period of time. The lack of fastness to light of artificial vermilion is, therefore, not proportional to the fineness of grain. The vermilions most fugitive in light are found amongst those prepared by the wet process. Out of fifty kinds, including three prepared in the dry way, 30 per cent. darkened very distinctly within four to five days. Out of fifty-eight samples of vermilion (of German and Austrian origin), mostly prepared in the wet way, only 30 per cent. remained unchanged during a period of six months; amongst these were those manufactured by the dry process, and the native vermilions. After a year only the sublimed and the native products showed very little or no change. In the case of certain carmine vermilions it was observed that the first signs of darkening which appeared on exposure to light diminished again in the dark, until the original shade was restored. Thus this light reaction also appears to be reversible as far as the first stage is concerned. If the darkening effect once becomes stronger, then the reaction begins to be irreversible. (*Cf.* Prussian blue.) As a general rule the darkening of vermilion in the light takes place superficially.

These phenomena have not yet been clearly explained. They depend either on local influences exercised by the vehicles employed, or on the presence of a modification of vermilion transformable with particular ease at the points affected. With regard to the former of these suggested explanations, the statement by Alsberg that vermilion rapidly becomes black when steam is passed over it, is of importance, and von Heumann has observed that this accelerating effect is also produced by ammonia and alkalis. Von Heumann also showed that when vermilion is rubbed on a sheet of copper the latter is blackened, copper sulphide being formed.

Behaviour in Mixtures (Fastness to Zinc White).—The numerous statements which have been made with regard to the double decomposition of vermilion with white lead and other lead colours are founded on error, so far as technically pure mercuric sulphide is concerned. Experiments have shown that:—(1) Vermilions containing free sulphur or alkali sulphides turn to a dark brownish-red when boiled with lead acetate solution, and also when warmed with pure white lead free from lead acetate. (2) Vermilions from which the sulphur has been extracted retain their colour when treated in the same manner. Mixtures of pure vermilions and pure white lead made into a thin paste with water, and allowed to settle, did not change colour during a year. After three years they had darkened superficially, but only through the transformation of the vermilion into the black modification.

Oil washes of mixtures of the pure pigments, kept in the dark, remained unchanged for six years.

The darkening of cinnabar in the light is not arrested by mixing it with white lead, zinc white, whiting, lithopone, or barium sulphate. Zinc white has, to a certain extent, a special effect. Washes made up from pale zinc white mixtures and gum arabic become distinctly grey within fourteen days, a change also observed in mixtures prepared with the other white pigments. Subsequently, however, the zinc white mixtures fade quite distinctly, apparently owing to oxidation of the vermilion.

Imitation Vermilions. (See under Red Lead, p. 961.)—A series of new coal-tar dyes of relatively high permanency in light (permanent reds, etc.) have rendered it possible to manufacture vermilion substitutes for painting signal colours, and for colour printing, wallpaper printing, etc., which, as regards fastness to light, fully satisfy requirements, and naturally do not exhibit the property of blackening. Among the mineral colours pale cadmium red in oil appears to be coming into vogue as a vermilion substitute, chiefly for artists' use.

Antimony Vermilion.

This pigment has lost its former importance in painting chiefly on account of the fact that the method of preparation is relatively complicated and the desired shade is not always attained. Kopp's method of preparation consists in decomposing calcium hyposulphite with antimony chloride, whilst Wagner employed solutions of tartar emetic, tartaric acid, and thiosulphate.¹ Antimony vermilion is an oxysulphide of the composition $\text{Sb}_6\text{S}_6\text{O}_3$. When properly prepared it possesses a pure red colour without any yellow or blue tinge but with a tendency towards a brown tint. When heated with sodium carbonate solution or lime water it darkens strongly, and is, therefore, not fast to lime. When treated with potassium hydroxide it becomes yellowish-red; when heated it blackens but does not sublime, and thus differs in this respect from vermilion. It differs from chrome red in being insoluble in strong potassium hydroxide solution, and it does not become yellow when digested with acetic acid. According to Mierzinski,² antimony vermilion is fast to light and air.

Cadmium Red.

This pigment, which has only recently come on to the market, is recognised by the colour of its powder, which differs from the very deep cadmium orange to which the name "cadmium red" is sometimes given. At present it is offered for sale in two shades, viz., pale and

¹ Cf. Zerr and Rübenkamp, *Colour Manufacture*, p. 282.

² *Handb. der Farbenfabrikation*, vol. i., p. 516.

dark cadmium red. Both varieties form dull powders of a colour somewhat resembling that of Pozzuoli earth, but when ground in oil they produce red tones of such warmth that these colours are now employed as vermilion substitutes and as artists' oil colours.

According to Eibner,¹ both varieties of the older cadmium red contain preponderating amounts of cadmium sulphide and small quantities of cadmium selenide, and, in addition, heavy spar as a diluent. The cadmium selenide is the component responsible for the shades of these colours. It is not yet known in what way these pure red shades, free from any yellow tint, originate; it may be assumed, however, that a chemical compound, an isomorphous mixture, or a solid solution of cadmium sulphide and cadmium selenide is present, and not merely a mechanical mixture. Experiments have shown that the heavy spar in these colours is in all probability present not as an adulterant, but as a substratum without which the respective shades could not be produced. Pure cadmium-selenium sulphide somewhat resembles caput mortuum in colour. The pale varieties of this kind of cadmium red contain about 76 per cent., the dark about 58 per cent. of barium sulphate. The most recent products of this nature contain no heavy spar. In these cases the excess of cadmium yellow acts as the substratum. According to the choice of substratum and the quantity of selenium present, shades varying from red to purple can be produced. Cadmium red cannot be employed as a water colour or distemper, since in these vehicles the necessary deepening in shade of the powdered pigment is not developed.

Qualitative Analysis.—On warming the cadmium red colours with dilute hydrochloric acid, sulphuretted hydrogen is first liberated; the colour then becomes dirty red and subsequently grey, and at the same time the radish-like odour is noticeable characteristic of the highly poisonous selenium hydride, which is also detected by the appearance of white clouds of selenious acid on igniting the gas. If this is passed into water or into aqueous sulphurous acid, red selenium separates out. On continued boiling, the pigment either dissolves completely, leaving only the insoluble heavy spar, or else selenium in the form of a grey powder remains with the latter. The varieties which contain no heavy spar leave behind only traces of selenium.

Quantitative Analysis.—A weighed portion of the substance is heated with nitric acid (sp. gr. 1.4) until it becomes white. The solution is diluted with water, allowed to stand for two hours, and the heavy spar then filtered off and estimated. The filtrate is concentrated and evaporated down with hydrochloric acid until the nitric acid is driven off. The diluted solution is treated with barium chloride, which precipitates the sulphuric acid as sulphate; in the filtrate selenium

¹ *Malmaterialienkunde*, p. 143.

is precipitated by saturating the solution with sulphur dioxide gas, and the precipitate is dried at 105° and weighed. After driving off the sulphur dioxide, sulphuretted hydrogen is passed into the filtrate, and the cadmium precipitated as sulphide, which is ignited in a current of sulphuretted hydrogen and weighed. L. Marino¹ has described a method for the volumetric estimation of selenious acid by means of permanganate.

Fastness to Light.—The cadmium reds appear to be quite as permanent in the light as the technically pure cadmium yellows. Water and oil colour washes underwent no change during a period of two years.

Behaviour in Mixtures (Fastness to Zinc White).—Cadmium reds, like the cadmium yellows, are incompatible with the arsenic greens. Two per cent. mixtures with zinc white in the form of water colour washes, under glass, faded very distinctly in a month.

Chrome Red.

This colour, the most basic lead chromate ($\text{Pb}_2(\text{OH})_2\text{CrO}_4$), is prepared on the manufacturing scale by adding a "cream" of white lead ground in water to a boiling solution of neutral potassium chromate, boiling the mixture strongly for eight or ten minutes until it attains a deep violet shade, allowing the resulting precipitate to settle, and washing it with boiling water. The product so obtained is dull in shade, and must be further treated with dilute sulphuric acid to convert it into true chrome red, after which it is washed to remove the acid. Another process, by which bright shades may be obtained, consists in adding a mixture of basic lead chloride and caustic soda to a boiling solution of potassium chromate, and washing the precipitate formed. In this case subsequent treatment with sulphuric acid is unnecessary. Dark shades cannot be produced in this way.

The great disadvantage in this pigment is its gritty crystalline form. When ground fine the colour is no longer dark red but more or less orange-yellow.

Chrome red finds its chief application as a substitute for vermilion in fresco painting. It can be mixed with oil, but separates again very quickly on account of its high specific gravity. It has the limited fastness of all lead colours.

By suitably influencing the formation (size) of the crystals very beautiful shades may be obtained, such as those sold under the names of "chrome garnet" and "chrome carmine." Other names applied to it commercially are "Persian red," "Derby red," "Vienna red," "Victoria red," "American vermilion," etc.

Chrome red dissolves in dilute nitric acid to a clear red solution, by

¹ *Z. anorg. Chem.*, 1909, **23**, 143; *J. Soc. Chem. Ind.*, 1909, **29**, 85.

which means it may be distinguished from red lead and vermillion. Treated with hydrochloric acid a green solution is formed containing a white precipitate of lead chloride.¹

VI. BLUE PIGMENTS.

The naturally occurring blue pigments, *Lapis lazuli* or native ultramarine, *Azurite* and the *Blue earths* (Vivianite, Ferrous phosphate), are seldom used.

The artificial blue mineral pigments in present use include the *Iron Cyanide Pigments*: Paris blues (Berlin blue), Turnbull's blue; the *Copper* and *Cobalt blues*; and the *Blue Ultramarines*.

Prussian Blues.

Berlin Blue, Paris Blue. Other designations are occasionally used, such as Steel or Milori, Antwerp, Mineral blue, etc.

The iron cyanide pigments may be looked upon as lying on the border line between the mineral and the organic pigments. Taking into account their origin and properties, they approach the organic lakes; they are ferric lakes of ferrocyanic acid.

The typical Prussian blue and the Berlin and Paris blues of commerce are still usually defined as identical substances. E. J. Parry and J. H. Coste² have pointed out that the pigments found on the market under the names "Prussian blue," "Berlin blue," "Paris blue," "Steel blue," "Milori blue," etc., are mixtures of ferric and ferric-potassium ferrocyanides, whereas the blue obtained from potassium ferrocyanide by the action of an excess of ferric salt in acid solution is ferric ferrocyanide free from potassium, and does not occur in commerce. The trade name "Prussian blue" is therefore a collective name. In fact these pigments differ considerably in chemical composition, hue, and stability.

According to L. Pelet-Jolivet,³ the most important technically pure commercial varieties of iron cyanide colours contain the following amounts of potassium and water:—

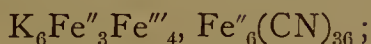
	Potassium. Per cent.	Water retained at 110°.
Steel blue	21.0	10.5 to 14.0
Steel blue with copper-like lustre	19.1	26.7
Prussian blue, ordinary	16.8	29.4 to 37.8
Prussian blue with copper-like lustre	15.4	33.6
Prussian blue, dark	12.25	42.0
Prussian blue (theoretical)	0.0	28.0 to 42.0

¹ Cf. Zerr. and Rübenkamp, *Colour Manufacture*, p. 273.

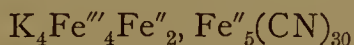
² *The Chemistry of Pigments*.

³ L. Pelet-Jolivet, *Theorie des Färbeprozesses*, p. 219.

According to C. Chérix,¹ Steel blue has the composition :—



and the insoluble Prussian blues the composition :—



with varying amounts of adsorbed water. (*Cf.* Turnbull's blue.) Since all the commercial varieties of Prussian blue described as insoluble in water are not quite insoluble, soluble Prussian blue, $Fe_5(CN)_{12}K_2$, must also be taken into account as a component part of these products. P. Woring² has recently advanced the view that Prussian blue is a ferrous ferricyanide.

Preparation.—According to Zerr and Rübencamp,³ the "direct process" of manufacturing iron cyanide pigments by precipitation of potassium ferrocyanide with excess of ferric salt solution is now only used for the preparation of a few varieties of Prussian blue, since the pigments obtained by this method cannot compare in beauty of shade with those prepared by the "indirect process."

Steel Blues and *Milori Blues* are manufactured almost exclusively by the indirect process, in which Berlin white (white paste), $FeK_2Fe(CN)_6$, is first prepared by the action of potassium ferrocyanide on ferrous sulphate. The product is then converted into the blue by various processes of oxidation. Formerly the oxidation was chiefly carried out by blowing in air. At the present time nitric acid, aqua regia, ferric salts, and, more frequently, chlorine derived from bleaching powder or potassium chlorate and hydrochloric acid are used. The process of formation of these blue pigments is still generally regarded as being represented by the following equations :—



As an expression of the formation of the Prussian blues these equations are inadequate if the hypothesis be admitted that the potassium-content is not due exclusively to adsorption, but is, in part, a component of the molecule, as must be concluded from the composition of Berlin white.

Soluble Prussian Blue was formerly obtained by treating a solution of potassium ferrocyanide in excess with ferric chloride. In the preparation on a technical scale sodium sulphate is added to the solutions of the reacting substances, whereby the colour is salted out. The precipitate is washed with water until the washing water begins

¹ *Etude sur les Bleus de Prusse industrielles*, Dissertation, Lausanne, 1908.

² *J. prakt. Chem.*, 1914, 84, 51; *J. Soc. Chem. Ind.*, 1914, 33, 148.

³ *Colour Manufacture*, p. 165.

to turn blue. Another method depends on the solubility in oxalic acid of Prussian blue insoluble in water. The initial precipitate is ground in the form of paste with crystallised oxalic acid in a mill, and, after some time, the mixture is dissolved in hot water. This pigment was formerly used as an ink for colouring paper and also in the dyeing of textiles. It could not be used in painting as it would stain the paper. Nevertheless, among the Prussian blue water colours there are some which are almost completely soluble in water.

Physical Properties of the Commercial Varieties of Iron Cyanide Pigments.—The varieties designated "Prussian blues" come into the market in deep blue oblong pieces which are very hard, dense, and tough, and exhibit a strong copper-like lustre both externally and on freshly broken surfaces. This lustre is said to be produced chiefly by the method used in drying (at first slowly at the ordinary temperature, then at 75° - 90°). It appears, however, that pressure is also employed. According to Zerr and Rübenkamp, these varieties are mostly prepared by the direct process.

The pigments known as "Steel blue" or "Milor blue," on the other hand, form dull rectangular pieces, very much lighter in colour than Prussian blue. The Steel blues are lighter than the Milori blues; both brands are of low density, fragile and friable. When ground, they assume only a very imperfect copper-like lustre. So far as is known, these varieties are manufactured exclusively by the indirect process. Intermediate between Prussian blues and Steel blues lie the "Bronze blues." Distinct differences in shade exist between the individual technical products. Besides the typical green-tinged blues other varieties occur possessing a violet tinge and dull shades. The colouring power of the iron cyanide colours is extraordinarily great; no other mineral pigment approaches them in this respect. On the other hand, they possess less colouring power than most of the blue coal-tar dyes. In addition, their character as glaze pigments is indicated by their pronounced glazing power, which property, however, is lost when they are applied in thick coats, on account of their power of absorbing light.

Fastness to Light.—The Prussian blues turn white on exposure to light. This action, which is reversible, is regarded by Eibner as due to reduction to Berlin white. The bleaching effect can be stopped immediately by treatment with moist chlorine, nitric acid fumes, or other acid oxidising agents, the blue colour being restored. The change is therefore due to a chemical reaction on which water exercises an accelerating effect. As water colours and in the unmixed state the Prussian blues occupy an intermediate position as regards fastness to light, under normal conditions of moisture. Church found that a water colour wash in dry air retained its full intensity during a period of four years. On the other hand, when enclosed in a glass tube with ordinary

air, it diminished, within thirteen months, from the intensity 10, as measured by Lovibond's tintometer, to intensity 1, and became sea-green in colour. He also observed that soluble Prussian blues were more unstable in the light than the insoluble varieties. An oil colour wash, on the contrary, became somewhat green after five years and only lost one-tenth of its original intensity. In the case of Prussian blue artists' colours, kept under glass, A. Eibner observed no diminution in intensity within two and a half years. Out of nineteen different commercial varieties of Prussian blue only one showed slight diminution in intensity of shade within eight months.

Sensitiveness to Zinc White.—The last-named varieties behaved quite differently when made up into pale mixtures with zinc white, and tested in the form of a wash with gum arabic. A. Eibner found that no coloured pigment exists which, under similar conditions, is altered so rapidly in the light by zinc white as the Prussian blues; 0.5, 2, 4, 8, 16, 32 and 64 per cent. mixtures of all known commercial brands of Prussian blue, Steel blue, Milori blue, etc., faded under glass in direct sunlight (August) within two hours to about half their original intensity, and, at the same time, turned very green. The restoration of the colour in the dark depends on the intensity of the tint and the duration of exposure to the light. The paler mixtures require four months to return to their original intensity of shade, but, for the most part, the green tinge persists. As in the case of other pigments, mixtures of Prussian blues with white lead, heavy spar, lithopone, or whiting suffer less, under the same conditions, than mixtures with zinc white. The protection which these diluents afford to the blues is very much less, however, than in the case of other coloured pigments.

In oil, the destructive action of zinc white on Prussian blues is very much less than when vehicles soluble in water are employed.

Compatibility in Mixtures. Fastness to Oil.—It has long been known that mixtures of Prussian blues and caput mortuum or vermilion in oil darken after a time. This is probably due, in the first place, not to chemical changes, but to separation of the mixture according to the specific gravity of the pigments. Washes of equal shade made from mixtures of Prussian blue and vermilion, in linseed oil and oil lacquer varnish respectively, behaved differently in that only the former darkened on drying. In this case the vermilion had time to separate from the Prussian blue in conformity with its specific gravity. It has recently been observed that slight double decomposition may take place between Prussian blues and pale cadmium yellows, with the formation of thiocyanates or of potassium ferrocyanide. The former resulted in the case of a cadmium yellow containing oxalate, and the latter with one containing cadmium carbonate.

Fastness to Lime.—All the iron cyanide colours are almost instantly

decomposed by alkalis, the typical Prussian blues forming ferric hydroxide and potassium ferrocyanide. This reaction serves for the qualitative detection of these pigments. Slaked lime behaves in the same way, but reacts more slowly. Hence the Prussian blues and all mixed colours such as chrome greens and zinc greens cannot be employed in lime or fresco painting. The decomposition by potassium hydroxide is represented by the equation:—



*Adulterated Varieties*¹ are those brands, sold under the names "Berlin blue," "Mineral blue," "Paris blue," and the older names "Hamburg," "New," "Erlangen blue." They contain additions of clay, heavy spar, zinc white, magnesia, gypsum, etc. The object of these additions is partly to lower the price, and partly to heighten the shade or produce covering power, as, for example, in the case of Mineral blue. These pigments, in the form of water colours, distempers, etc., are not so fast to light as the untreated Prussian blues.

Antwerp Blue is a mixture of iron and zinc ferrocyanides. It has a violet shade and is duller and covers better than Prussian blue. *Washing Blue* consists of Prussian blue mixed with starch meal.

Analysis. (1) *Technically pure Prussian Blues.*—Since commercial Prussian blues, almost without exception, contain potassium, the estimation of the latter is of importance. E. J. Parry and J. H. Coste² incinerate the pigment, dissolve the weighed ash in hydrochloric acid, filter off any insoluble matter, precipitate the iron and alumina with ammonia, and after weighing the mixed oxides reduce the iron with stannous chloride and determine it with permanganate; the aluminium is estimated by difference. After driving off ammonium salts the alkali (in combination as chloride) is determined in the filtrate by titration with silver nitrate. The sulphuric acid is estimated in a separate portion of the filtrate. From the figures thus obtained—the weights of alkali salts, hydrochloric and sulphuric acids—Parry and Coste were able to establish the fact that, in all cases, the alkali metal was practically all present as either potassium or as sodium, and never

¹ There appears to be a well-established distinction in Germany between the *pure* and *adulterated* Prussian blues, the former being sold under the name of "Paris blue," and the latter being known as "Berlin blue," although, when referring to pure Prussian blue in a strictly chemical, as apart from a commercial sense, the name "Berlin blue" is frequently used. In England, unfortunately, no such distinction is drawn, and there exists accordingly absolute confusion in the nomenclature of the Cyanogen blues so far as concerns any indication as to their purity or otherwise. The only term which appears to be generally employed to designate the adulterated colour is "Brunswick blue," but the same mixture may just as probably as not be sold under the name "Paris," "Prussian," or "Berlin." In this section the name "Prussian" has been used in all cases when referring to the Cyanogen blues, as being probably the most commonly employed in England.—H. J. L. RAWLINS.

² *Analyst*, 1896, 21, 225.

as a mixture of the two metals. Another weighed amount of the pigment is boiled for some time with potassium carbonate, and the ferric hydroxide obtained dried, ignited, and weighed. The resulting weight multiplied by 0.7 gives the iron other than that present in the radicle. Small amounts of aluminium (1-3 per cent.) were found by Parry and Coste in most of the Prussian blues; this, they state, is not to be looked upon as an adulteration, alum being frequently added as a precipitant in the preparation of these pigments. In some cases potassium ferrocyanide was found to be present, and could be washed out. According to B. Dyer,¹ the nitrogen is estimated by the method of Kjeldahl, Gunning, and Arnold. The sulphuric acid should not become blackened during the determination; if coloration takes place, then, according to Parry, foreign organic matter is present.

The determination of moisture is carried out at 100°. According to Williamson, the total water-content is best determined by combustion with lead chromate. Parry and Coste state that a pure Prussian blue should contain about 20 per cent. of nitrogen and 30 per cent. of iron, calculated on the dry substance. A "dry" blue should contain under 7 per cent. of water.

Church carries out the qualitative examination for alkali by incinerating the pigment and testing the aqueous extract with turmeric paper. If a Prussian blue contains potassium ferrocyanide, the potassium from the latter will also be present in the ash as potassium cyanide. In this case Church recommends extraction with hot dilute hydrochloric acid, whereby the potassium ferrocyanide is dissolved. According to Zerr and Rübencamp, the Milori blues often contain tin compounds. (Cf. Turnbull's blue.)

(2) *Adulterated Prussian Blues*.—For the detection of adulterants advantage is taken of the action of alkalis on the ferrocyanides, either by filtering off the ferric hydroxide obtained, dissolving it in sulphuric acid, and titrating the reduced solution with permanganate; or by determining the potassium ferrocyanide formed, according to Lunge and Schäppi's modification of Hurter's method. (Cf. Vol. I., p. 427.) In both cases the quantity of pigment found is compared with the quantity contained in a technically pure Prussian blue.

Another method of determination is that of M. Dittrich and C. Hassel,² which is carried out as follows:—The blue is decomposed into ferric hydroxide and sodium ferrocyanide by boiling with pure sodium hydroxide. When the reaction is complete the ferric hydroxide is filtered off, well washed, the filtrate treated with 30-40 c.c. of 10 per cent. ammonium persulphate solution, acidified with dilute sulphuric

¹ *J. Chem. Soc.*, 1895, 67, 811.

² *Ber.*, 1903, 36, 1932. Also, C. Coffignier, "Verfahren zur Bestimmung von Berliner Blau," *Bull. Soc. Chim.* [3], 1904, 31, 391; *J. Soc. Chem. Ind.*, 1904, 23, 456

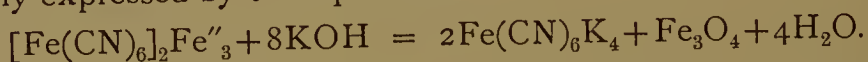
acid, and heated until all the sodium ferrocyanide is decomposed. The two iron precipitates must be dissolved again and reprecipitated, as a large quantity of alkali adheres to them.

The qualitative determination of the mineral admixtures is carried out according to the method of Bolley-Stahlschmidt,¹ by first decomposing the cyanogen compounds. 2 g. of the Blue are mixed with an equal weight of ammonium nitrate and three times the weight of ammonium sulphate, and the mixture heated in a small tubular retort provided with a receiver but not luted to it. All basic compounds, with the exception of ammonia, remain in the retort. The residue is warmed with water slightly acidified with hydrochloric acid, in which heavy spar, gypsum, clay, and sand remain undissolved, and the separate constituents of the hydrochloric acid solution and of the insoluble residue identified by the usual tests.

Turnbull's Blue (insoluble) is formed by the action of a ferrous salt in excess on potassium ferricyanide. It was first prepared by Gmelin, and was then considered to be ferrous ferricyanide formed according to the equation:—



On warming it with alkalis, however, potassium ferricyanide is not regenerated, only potassium ferrocyanide and a mixture of hydrated ferric and ferroso-ferric oxides being formed. This reaction was formerly expressed by the equation:—



K. A. Hofmann² is of opinion that an interchange in the degrees of oxidation of the iron takes place in this decomposition. E. Müller and T. Stanich³ found that freshly prepared Turnbull's blue is, in fact, a ferrocyanide, but is not identical with Prussian blue, since ferrous iron is also present apart from the radicle, together with potassium and ferric iron, and as a result of their investigations suggested the following formula:—



Experiments by A. Eibner, which were confined to the object of gaining information as to differences in colour, fastness to light and miscibility of Prussian and Turnbull's blues, proved that freshly prepared Turnbull's blue which has been rapidly washed is not identical with the typical Prussian blues, either in shade or as regards stability to light and vehicles. It possesses an ugly tone resembling that of indigo, and when made up as a water colour wash of deep shade it fades very

¹ *Handbuch der tech. chem. Untersuchungen*, 6th ed., p. 295.

² *Annalen*, 1904, 337, 1; 1905, 340, 267; 1905, 342, 364; *J. Soc. Chem. Ind.*, 1904, 23, 1209; 1905, 24, 1221.

³ *J. prakt. Chem.*, 1909, 79, 81.

markedly within three weeks. This reaction is reversible. The longer it is in contact with air during the process of washing, the more stable to light does it become. The behaviour of Turnbull's blue with zinc white is essentially different from that of Prussian blue. Moreover, it is more sensitive towards organic vehicles than the latter.

The soluble modification of Turnbull's blue, when treated with various metallic salts, especially those of tin, forms particularly beautiful, insoluble, blue compounds. An exceptionally fine Turnbull's blue containing tin can also be obtained by mixing together solutions of potassium ferricyanide and a ferric salt, with addition of stannous chloride.

The presence of tin in Turnbull's blue may be detected by fusing the latter with a mixture of sodium carbonate and saltpetre, and dissolving the melt, which contains the tin as sodium stannate, in hydrochloric acid. The solution is filtered, if necessary, and treated with sulphuretted hydrogen, when tin sulphide gradually separates out.

Turnbull's blue cannot be employed as an artists' pigment, on account of its instability and dull shade. Nevertheless, according to Church, it forms a component part, together with soluble Prussian blue and ferric ferrocyanide containing potassium, of many commercial Prussian, Steel and Milori blues, and is the cause of their instability in the light. The same ideas are expressed in Chérix's formulæ for Prussian and Steel blues (p. 969), according to whom it would appear that, in the oxidation of the "white paste," complete conversion of the iron outside the radicle into the ferric state does not always take place. On the other hand, Eibner, on examining a considerable number of commercial Prussian and Steel blues, found no ferrous iron, whereas the latter was present in all Turnbull's blues, whatever the method of preparation.

Freshly precipitated Turnbull's blue made up as a wash with gum arabic is very much more unstable than the Prussian blues. Test portions faded within three weeks to about half the original intensity, and became sea-green in colour. In the dark, or under the influence of acid oxidising agents, this reaction is reversed. As in the case of the Prussian blues, the change is therefore brought about by reduction, but in this case in the ferric iron portion outside the radicle.

Blue Copper Colours.

These artificial pigments consist essentially of cupric hydroxide, the pale and somewhat greenish shade of which depends on the method of manufacture. They are for the most part durable in lime, hence the name "*Lime blue*"; on the other hand, they are not applicable as oil colours, since they turn green in oil, forming copper salts of fatty acids. During recent years they have been largely displaced both by ultramarine

and by the coal-tar colour lakes. They are still used for painting exteriors, in house painting, and in distemper.

Mountain Blue.—This name has been transferred from the mineral “azurite” to the artificial product, although the latter does not possess the same composition as the mineral. The colour is prepared from cupric chloride obtained by the action of calcium chloride on copper sulphate; the cupric chloride is treated with lime paste, which produces green copper oxychloride, and the latter is then converted into the blue colour by adding potassium carbonate and milk of lime.

Lime Blue is prepared in a similar manner, but in one operation, by precipitating a solution of copper sulphate with milk of lime, with addition of ammonium chloride. It consists of cupric hydroxide, mixed with lime. Lime blue sold in the form of oblong rectangular lumps is known as *Neuwied blue*. The name “lime blue” is also applied to the lime-fast blue coal-tar colour lakes and to ultramarine cheapened by the addition of gypsum.

Bremen Blue is manufactured by the “direct process” as follows:—Green basic copper sulphate is precipitated by treating a solution of copper sulphate with sodium carbonate solution of sp. gr. 1.075, and the product is converted into the blue by further treatment with a more concentrated solution of sodium carbonate of sp. gr. 1.26. In the “indirect process” a solution of copper sulphate is mixed with common salt, scrap copper, and caustic soda, the mixture placed in oxidation boxes, and left to react in the presence of air for several months, whereby green cuprous oxychloride is formed. The product, after being passed through a sieve to remove unoxidised particles of copper, is then treated with a definite quantity of hydrochloric acid, and finally converted into the blue by means of caustic soda at a temperature not exceeding 30°–35°.

Adulterants which occur in these copper colours comprise gypsum, ground pumice-stone, infusorial earth, etc. The analysis is carried out by the usual methods, and includes the estimation of copper and water, and also the amount of additions.

Oil Blue.¹—This pigment, which is a specially prepared form of copper sulphide, is applicable as an oil colour. It is manufactured by introducing copper filings into boiling sulphur; after cooling, the mass is boiled with caustic soda in order to remove the excess of sulphur. This colour is unaffected by sulphuretted hydrogen, but it can only be used in linseed oil varnish, as it becomes oxidised in other vehicles.

Blue Cobalt Colours.

These colours consist essentially of glass fluxes or alumina (cobalt aluminates with alumina) coloured blue by cobalt oxide; hence

¹ The name “Oil blue” is also applied to Prussian blue.

they approximate to the native substratum pigments (ochres, etc.). For their preparation cobalt salts, or roasted cobalt ores known as "zaffres," are employed.

Smalts.

This colour is a cobalt silicate containing potassium, and is obtained by fusing *zaffres*¹ with quartz sand and potassium carbonate in a glass-furnace. The potassium carbonate cannot be replaced by sodium carbonate, as cobalt sodium glasses never give a pure blue colour, but one possessing a red or brown shade. Smalts contains about 65-72 per cent. silica, 2-7 per cent. cobaltous oxide, 2-22 per cent. potassium, and about $\frac{1}{2}$ -20 per cent. alumina. It also contains small quantities of lime, iron, and nickel, and, in most cases, arsenious acid, which was formerly added purposely as it increases the beauty of the colour. Nickel is a particularly harmful impurity of zaffres, as it imparts a violet tinge to the smalts. Bismuth is almost as detrimental, causing the glass to become greenish-blue. Iron in any great quantity is also to be avoided, as it produces a dirty appearance in the product.

Smalts, being a kind of glass, has poor covering power, and has been displaced by ultramarine and cobalt blue, practically its only use at the present time being for painting earthenware, and as a blueing and bleaching agent where a permanent effect is required. Smalts is only slightly attacked by acids, but, like all glasses, it is not quite stable towards alkalis. It differs from cobalt blue also, in being fusible.

The methods of *Analysis* are described under cobalt blue.

Cobalt Blue.

(Thénard's Blue; Cobalt Ultramarine; Azure Blue.)

Cobalt blue is prepared, according to Leithner, by calcining a mixture of cobalt nitrate and alumina, or by mixing a solution of alum with a solution of a cobaltous salt, treating the mixture with alkalis, and calcining the precipitate obtained. Thénard calcined a mixture of aluminium hydroxide and cobaltous phosphate or arsenate.² The presence of phosphoric acid favours the formation of the colour and increases its beauty.

The cobalt blues are generally described as cobalt aluminates, but the commercial brands contain, according to the shade, varying amounts of cobalt (between 19 and 30 per cent.), the highest of which does not reach the theoretical content, viz., 36.6 per cent. for cobalt aluminate.

¹ For the better qualities oxide of cobalt is used.

² *Dingl. polyt. J.*, 1834, 53, 447; 1836, 54, 339; also, A. Munkert, *Die Normalfarben*, p. 113.

Moreover, the cobalt blues prepared from phosphates are constituted differently from those containing no phosphates. Accordingly, the designation as aluminates applies, approximately, only to the dark varieties prepared without phosphoric acid. W. Stein¹ considers the cobalt blues to be molecular mixtures of alumina and cobalt oxide. (*Cf.* Ultramarine.)

Two brands of cobalt blue are usually found in commerce, viz., pale and dark, which differ in the amount of the colouring principle present. The cobalt blues are insoluble in dilute acids and alkalis, and are only decomposed by fusion with alkali. The covering power is small. Like the blue ultramarines they have a dirty violet appearance in artificial light. In art painting they are employed as oil and water colours for colouring porcelain, and for printing bank-notes in countries where a blue is used for this purpose, as such print cannot be reproduced by photographic processes.

They are perfectly fast to both air and light. When made up with zinc white as a water colour, however, they fade distinctly within two months.

Analysis.—A. Munkert² reduces the pigment, in the absence of phosphoric and arsenic acids, by heating in a current of hydrogen, dissolves the black mass in hydrochloric acid, and separates the cobalt from the alumina by means of sodium acetate. If the acids mentioned are present, the pigment is fused with six times its weight of potassium carbonate, the melt extracted with water, the solution filtered off, and the insoluble residue subjected to further fusion with potassium carbonate until it is completely decomposed, when it is again extracted with water and filtered. The decomposition can be effected in a single operation by fusing with ten times the weight of alkali hydroxide in a silver crucible. The combined filtrates are acidified with nitric acid, and evaporated to dryness. After taking up the residue with water, the aluminium is precipitated together with phosphoric and arsenic acids and silica, by means of ammonium hydroxide. Silica is separated by dissolving the precipitate in nitric acid, evaporating down the solution, extracting with water, and filtering. The filtrate is evaporated down with sulphuric acid to remove the nitric acid, and is then treated repeatedly with ammonium sulphate and alcohol, whereby the aluminium is separated out as aluminium ammonium sulphate. The precipitate is washed with alcohol, ignited, and the aluminium estimated as Al_2O_3 . After evaporating off the alcohol, arsenic is precipitated as the sulphide in the combined filtrates, and after filtration, the phosphoric acid precipitated with ammonium molybdate.

The black residue obtained after fusion consists of crystalline spangles of cobaltous oxide. If the estimation of the very small traces

¹ *Dingl. polyt. J.*, 1871, 201, 420.

² *Normalfarben*, p. 116.

of nickel, iron, and copper contained in the residue has not to be carried out, the latter, after thorough washing, may be reduced directly according to Rose's method, ignited a second time in the current of hydrogen, washed in order to remove alkali, and weighed as metallic cobalt.

Cæruleum.

(Cerulean Blue; Bleu Céleste.)

This colour is manufactured by calcining a mixture of cobaltous sulphate, tin salt, and chalk, the tin thus taking the place of alumina in the cobalt blues. Cæruleum has a more greenish tinge than the latter; hence its shade remains unchanged in artificial light. Its average composition is 50 parts stannic oxide, 18 parts cobaltous oxide, and 32 parts gypsum. It covers better than the cobalt blues and is used almost exclusively as an artists' colour.

Green-blue Oxide is an artists' pigment which has recently come on to the market. It is manufactured by calcining a mixture of chromic oxide, alumina, and cobalt salt. It covers better than cobalt blue.

Manganese Blue is produced, according to Bony,¹ by a process of calcination very similar to that used in the manufacture of ultramarine. A mixture of China clay, oxides of manganese, and barium nitrite, approximately in the proportion 2 : 3 : 8, is heated to redness in an oxidising atmosphere; compounds of iron must be excluded. The pigment is obtained in several shades varying from violet to sky-blue, but up to the present it has found little application.

Ultramarine.²

(Lapis Lazuli Blue (for Native Ultramarines); Oriental Blue.)

The ultramarines differ from all other inorganic pigments in as much as they cannot be valued by chemical analysis, the colouring principle not being present in a form which has proved capable of being dealt with by analytical methods. The quantitative estimation of all the individual constituents of the different commercial brands of blue and other coloured ultramarines does not, therefore, form a basis for the drawing of definite conclusions as to the quality of products similar to one another in shade. Such an estimation, where it is not concerned with the identification of foreign admixtures, is, therefore, less important than practical tests as to the stability and compatibility of the products in mixtures with other pigments. The question as to the material and technical identity of artificial blue ultramarines with

¹ *Farben-Zeit.*, 1907, 13, 77.

² Cf. R. Hoffmann, *Ultramarin*, 1902. Knapp and Ebell, *Dingl. polyt. J.*, 1878, 229, 69, 173. Heumann, *Annalen*, 1871, 199, 253; 1872, 201, 262; 1872, 203, 174.

native lapis lazuli cannot be answered so long as the composition of the two substances is incompletely explained. The investigations into the nature of the colouring principle of lapis lazuli and of the blue ultramarines respectively have extended over a long period. In the seventeenth century it was believed to be due to the presence of copper; Marggraf held that iron was the colouring metal; Walerius and Guyton considered that silver and ferrous sulphide respectively were the substances responsible for the colour, whilst Gmelin showed that the colour was not due to iron. Until quite recently it was assumed that the colouring principle was a definite chemical compound of constant composition. Stein (1871) considered that the black modification of aluminium sulphide was this colouring principle, which appeared blue in the cloudy medium of the white mother substance; more recently K. A. Hofmann and W. Metzener¹ have advanced the view that the blue sulphur sesquioxide of R. Weber² bears a relation to the chromophore of the blue ultramarines. It has since been assumed that particular physical conditions of the sulphur are the cause of the colour exhibited by the blue ultramarines. Lately, it has been thought that the solution of the problem is to be found in the assumption that the sulphur in a state of vapour is dissolved or adsorbed, and in this condition is able, like iodine, to assume different colours according to the nature of the receptive medium.³

The occurrence of the purple-red selenium and the green tellurium ultramarines of Guimet,⁴ of the organic ultramarines of de Forcaud⁵ and of the older silver ultramarines, points to the fact that the colour principle of the blue ultramarines contains groups which can undergo substitution.

Quite recently the older researches on the replaceability of the individual elements occurring in the ultramarines have been supplemented in an interesting way. Rohland,⁶ by heating talcs with sodium carbonate and sulphur, obtained green compounds which behaved like ultramarine, but the coloured component of which could be extracted with water. Notelle and Corblet⁷ observed that the silica used in the preparation of ultramarine only plays a mechanical part, and they attempted to replace it by other substances; they thus succeeded in obtaining a larger yield of pigment of considerable strength of colour. F. Singer has prepared green to greenish-blue pigments of the nature of ultramarine by heating or fusing zeolites with alkali sulphides.⁸

An account of the boron ultramarines, together with a discussion

¹ *Ber.*, 1905, 38, 2482; *J. Soc. Chem. Ind.*, 1905, 24, 898.

² *Pogg. Ann.*, 1875, 156, 531.

³ R. Rohland, "Ueber das Farbproblem des Ultramarins," *Phys. Chem. Zentr.*, 1908, p. 514.

⁴ *Bull. Soc. Chim.*, 1902, 27, 480; Morell, *ibid.*, 1902, 28, 522.

⁵ *Comptes rend.*, 1879, 88, 30.

⁶ *Loc. cit.*

⁷ *Farben-Zeit.*, 1909, 15, 1199.

⁸ Ger. Pat. 221344 of the 17th July 1909.

of the most recent views as regards the nature of the colouring principle in the silica ultramarines, has been published by J. Hoffmann.¹

The researches on the constitution and the colouring principle of ultramarines, even if they have not solved the problem, have at any rate led to the conclusion that these bodies are not individual coloured substances like, for example, cinnabar, whose colour is mainly dependent on the constant relative proportions by weight of its components, but that they contain a still unknown colour principle which is firmly held by a non-coloured basis, somewhat in the same way as the coloured components in the organic colour lakes. In both cases the problem as to whether it is a question of chemical combination or of adsorption is still unsolved. From the researches made up to the present, it follows that the technically pure unadulterated ultramarines must, without doubt, be looked upon not as "primitive pigments" but as "substratum pigments." The adulterated qualities are produced by the addition of gypsum, chalk, etc., as diluents.

Chemical Analysis.—The analytical control of the ultramarine manufacture comprises the analysis of the raw materials, the control of working conditions, and the examination of the finished product.

The losses in the manufacture of ultramarine are still great; in the burning process alone they amount to about 40 per cent., so that from the original mass 60 per cent. or at most 65 per cent. of raw product is obtained, and the latter, when washed, loses 20-25 per cent. and even up to 30 per cent. of soluble salts. The yield of finished blue from the original mass, taking an average of many years' experience, amounts to 48-50 per cent.

There is no doubt that these losses will be reduced, whether on chemical or on technical lines, and a higher yield obtained. In this connection a wide field is still open for investigation; in addition, means for utilising the escaping sulphuric and sulphurous acid gases are to be desired.

I. THE ANALYSIS OF RAW MATERIALS.

The raw materials comprise :—Clay, silica, sulphur, sodium carbonate, sodium sulphate (Glauber's salt), rosin and pitch.

1. Clay.—This forms the basis of the ultramarine manufacture. Everything may be said to depend on its quality and proper condition. It is used either in the raw or in the finely levigated state, in both cases either calcined or uncalcined. Levigated clay is usually preferred, as it gives a purer colour. The shade of colour is also dependent on the previous calcination of the clay. Calcined clay is more easily decomposed by sodium carbonate, and the free silica contained in the calcined variety is rendered more easily capable of reaction, as during the

¹ *Chem. Zeit.*, 1910, 34, 821; *J. Soc. Chem. Ind.*, 1910, 29, 1066.

burning process the specific gravity of the quartz decreases, amorphous silica being formed; this uncombined silica is thereby increased in volume, becoming loosened as it were, and gaining a greater surface for chemical action. If, however, the clay is too sharply burnt, this advantage of easier decomposability is lost, on account of the shrinkage or sintering which takes place. Clays which on ignition are rendered very red must be discarded, as they give a dull colour.

*The Physical Examination of the Clay.*¹—This comprises elutriation for ascertaining the quantity of admixed sand, the determination of the specific gravity and refractoriness or fusibility, and the examination of the contractibility.

The Schumann volumeter (Vol. I., p. 698) is, according to J. Aron,² not suitable for determining the specific gravity of clays, the results varying from those of the pyknometer because the air is not completely expelled; it is, moreover, difficult to introduce the clay into the apparatus.

The Chemical Analysis of Clay.—This is chiefly a question of determining the free and combined silica, since the preparation of any particular kind of ultramarine must be regulated by the ratio of the free and combined silica to one another, as well as to the alumina. The latter ratio must be greater in the case of soda ultramarines stable towards acids, than for sulphate ultramarines.

The analysis is carried out as follows:—The sample of clay is first powdered as finely as possible and sifted, using the greatest care, as the agreement of analyses depends to a great extent upon this operation. The amount of water present is determined by igniting until the weight is constant. A further quantity of about 1 g. is heated for about twenty hours with concentrated sulphuric acid in a covered platinum crucible until the acid fumes distinctly, the residue is taken up with water, washed two or three times by decantation, again transferred to the platinum crucible, and, after removal of the water present, heated for a further twelve hours with concentrated sulphuric acid as above. The contents are then added to the acid and washings of the first operation, diluted with water, and filtered.

The total silica remains on the filter paper; it is washed off with water, boiled with potassium hydroxide, and the resulting solution diluted and filtered. The filtrate contains the chemically combined silica, and the residue consists of the free silica (sand). The filtrate from the total silica is evaporated completely to dryness in a platinum dish, in order to drive off the excess of sulphuric acid, the residue is dissolved in water, and the aluminium precipitated with ammonia. The solution, with the precipitate in suspension, is evaporated completely

¹ Cf. the section on "Clay," Vol. I., pp. 569 *et seq.*

² Private communication to Prof. Gnehm.

to dryness on the water-bath, the residue taken up with water containing ammonia, and filtered; the precipitate of alumina is thus obtained in such a condition that it is easily and conveniently washed. In the filtrate, calcium, magnesium, and the alkalis are estimated in the usual way; as a rule, however, the last determination is unnecessary. The total silica is also determined by decomposing with alkali carbonate.

2. Silica.—The forms employed are:—Very finely ground quartz sand, infusorial earth, and the silica obtained from the manufacture of aluminium sulphate. The first of these is always pure, but is not usually ground sufficiently fine. The examination for fineness, which is very important, is carried out by suspending a weighed quantity in water, and filtering the whole through a small sieve composed of the finest silk gauze (about 160 meshes to the inch). A quartz sand which, after this treatment, yields more than 0.5 per cent. of residue at the most should not be employed. The infusorial earth must be well levigated, as otherwise it still contains too much loamy matter, and it must be completely dried before use. This form has, however, the great disadvantage of rendering the mixture too voluminous. The third variety of silica named above may still contain fairly large quantities of sulphuric acid, a factor which is not, however, an important consideration. The following is an analysis of this form of silica:—

	Per cent.
Loss on ignition	7.45
Silica	79.14
Alumina	7.92
Ferric oxide	1.20
Sulphuric acid (H_2SO_4)	3.02

Arsenic may also be present in greater or lesser quantities.

3. Sulphur.—Crude or recovered sulphur either in sticks or lumps is employed. Crude sulphur is examined for mineral impurities by burning a fairly large weighed quantity and weighing the residue. A sample which yields more than 2 per cent. of residue at the most should be absolutely discarded. Crude sulphur which is not pure yellow, but has a greyish-brown tint, should not be employed, as sulphur of this appearance is much harder to powder than the pure yellow form. Recovered sulphur often contains considerable quantities of cyanogen compounds, which, although not reacting in any way, are, according to E. Büchner, the cause of the small crystals which often appear in raw ultramarine.¹

It is also advisable to test the sulphur occasionally for arsenic. For this purpose 50 g. are extracted with ammonia, the solution precipitated with acid, the precipitate again dissolved in a little ammonia, and again precipitated with acid. If no appreciable quantity of arsenic sulphide is formed, then the sulphur may be taken as sufficiently pure.²

¹ *Dingl. polyt. J.*, 1878, 229, 433.

² *Cf.* also Vol. I., p. 267.

4. Sodium Carbonate.—Both Leblanc and ammonia soda are used. In regard to the latter, the view was at one time widely held that it was unsuitable for the manufacture of ultramarine; since, however, the Solvay works have manufactured a double-calcined and consequently “heavy” ammonia soda (sp. gr. 1.2-1.5 compared with 0.95 of the ordinary “light” form¹), it has been extensively employed. At the same time, the method of manufacture of the ultramarine, whether in muffle or crucible ovens, and the mixture itself must be considered in connection with the choice of the sodium carbonate. Certain varieties are better prepared with Leblanc soda, others with ammonia soda. The presence of a certain quantity of caustic soda in the Leblanc soda has, under some circumstances, a very favourable influence.

The strength of the soda also plays an important part, and soda of high percentage (of carbonate), weakened by the addition of sodium sulphate, produces an ultramarine entirely different from that made with soda of equally low strength in the first instance—that is, a soda in which the carbonate and sulphate are in the same relative proportions as in the artificially weakened, high-strength soda. In the originally weaker soda the disposition of the sulphate and carbonate molecules is certainly different from, and more intimate than in that artificially weakened by addition of sulphate.

The examination of the soda is carried out by the methods given in detail in the section on “Sodium Carbonate,” Vol. I., pp. 419 *et seq.* In the case of ammonia soda the contractibility or the specific gravity must be ascertained, in order to make certain that it is “heavy” soda.

The contractibility is tested by filling a large platinum crucible up to a certain mark with the soda, and observing if, after strong heating, any considerable decrease in volume has taken place.

The specific gravity of “heavy” ammonia soda is determined most simply by the methods described in Vol. I., p. 453. Another, though more tedious method, is to fill a leaden vessel, of about 1 litre capacity and of ascertained weight and volume, up to the rim with the sample; it is essential to introduce the soda in small portions at a time, and to press each down as firmly as possible before filling any further. Finally the soda above the rim of the vessel is scraped off with a glass plate, the whole weighed, and the specific gravity calculated. With a little practice “heavy” ammonia soda can be distinguished from “light” soda by the distinctly heavier feel on taking up a handful of the sample in question.

It is also necessary to determine by titration the amount of sodium chloride contained in the soda: soda containing more than 2 per cent. of sodium chloride must be absolutely discarded.

¹ By specific gravity, the weight of the closely packed carbonate is understood, as defined in the section on “Sodium Carbonate,” Vol. I., p. 453.

5. Sodium Sulphate (Glauber's Salt).—In many ultramarine works this is recovered from the lyes obtained in washing the raw ultramarine. The examination is carried out according to the ordinary methods. It is advisable only to employ an acid-free, calcined quality of a fine white appearance.

6. Rosin and Pitch.—These are tested for mineral impurities by the combustion of a fairly large quantity, as in the examination of sulphur.

The so-called Lesmahagow coal has recently been employed as a reducing agent, but the difficulty in reducing it to a fine state of division, consequent upon its great hardness, is a disadvantage.

It is also advisable to test the reducing power of these agents by means of litharge—*e.g.*:—

1 g. Rosin reduces	.	.	19.2 g. lead.
1 g. Pitch reduces	.	.	27.5 g. „
1 g. Lesmahagow coal reduces	.	.	21.8 g. „

II. CONTROL OF WORKING CONDITIONS.

Supervision of the Burning Process and Working up of the Raw Product.—In the manufacture of ultramarine the raw materials are ground as finely as possible, sieved, and mixed together in accurately weighed proportions. The mixture is again ground, and then burnt in crucibles or in a muffle. The greatest care must be used to obtain as uniform and fine a mixture as possible, and for the production of a good uniform raw product it is very essential that the quantity of mixture necessary for filling a muffle should be mixed in one operation. To make certain as to the correct composition, uniformity, and fineness of the mass, samples are taken from different parts, and the amount of soda present in each is determined. Samples are also examined on a silk sieve (about 150 meshes to the inch), through which everything should pass.

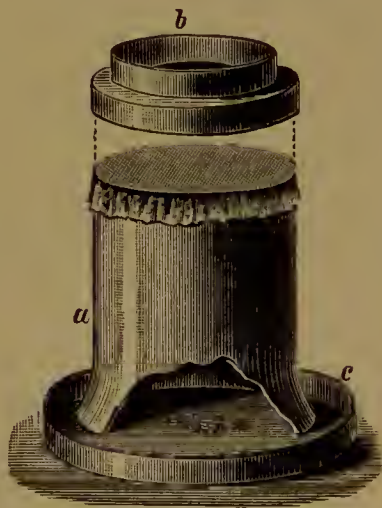


FIG. 96.

For testing the fineness in this way the following contrivance can be recommended as very practical:—The vessel (Fig. 96), which is made of tin, consists of two parts, *a* and *b*, and between them is placed the silk sieve, which becomes tightly stretched when *b* is fixed on to *a*; *b* has a rim about 1 cm. high and is occasionally furnished with a tightly fitting lid. The whole apparatus stands on a tin plate, *c*. The substance to be tested is brought on to the sieve and brushed through, either with

a somewhat stiff brush or with the finger ; or the sifting operation may be carried out by fixing on the lid and tapping it.

The burning process is the most important and most difficult operation of the whole manufacture. Given correctly proportioned ingredients and good, even charging of the mixture, the obtaining of a faultless product depends, above everything, on the burning. The correct management of the burning process is still almost entirely a matter of experience. The completion of the process is ascertained by taking out samples from the oven at definite times.

It is expedient also to follow the course of the process by gas-analysis, for in this way reliable inferences can be drawn as to how the operation is proceeding. The amount of oxygen is ascertained by means of Bunte's¹ or Orsat's² apparatus, and the sulphur dioxide by Reich's apparatus.³ For the determination of carbonyl sulphide, COS, which, according to E. Büchner's experiments, appears to be given off in large quantities during the formation of ultramarine, no suitable method has been proposed.

It is also useful to take measurements of temperature.⁴

After the burning process, the oven is closed and allowed to cool slowly ; the raw blue product is then taken out, sorted into qualities, and each quality separately worked up further. The raw product is freed as completely as possible, by lixiviation, from sodium sulphate, after which it is ground while wet, and levigated. Sodium sulphide, which is present, sometimes in larger, sometimes in smaller quantities, is very difficult to remove. If the washing water contain iron, sodium-iron sulphide is formed, which adheres even more persistently to the raw blue.

Under certain circumstances, in the muffle burning process, the undesirable by-products yellow and red ultramarine are obtained.⁵ E. Büchner has observed that the washing water from yellow and red ultramarine gives a fairly heavy precipitate with ammonia and a strong reaction for iron with potassium thiocyanate, while neither reaction takes place in the washing water from blue ultramarine obtained from the same oven.

It is important to make occasional laboratory determinations of the salts removable by washing from the different qualities of raw blue. From a quantity powdered in a mortar, 10 g. are weighed out and washed in a tared filter paper with warm water until barium chloride no longer produces a turbidity in the wash-water ; 500 c.c. of water are sufficient for the washing. The funnel is then placed in a drying chamber, and, when dry, the colour, together with the filter

¹ Cf. Vol. I., p. 195.

² *Ibid.*, p. 198.

³ *Ibid.*, p. 300.

⁴ Cf. *Dingl. polyt. J.*, 1876, 221, 471 ; and 1879, 232, 429.

⁵ Cf. Scheffer, *Ber.*, 1883, 16, 1450.

paper, is weighed, and the weight deducted from their combined original weights. The resulting loss, multiplied by 10, gives the percentage of soluble salts. For making several determinations at the same time, and where speed in arriving at the results is an object, the filtering apparatus shown in Fig. 97 proves very useful.¹ The glass cylinder *a*, which is open above and below and has ground edges, stands on a ground-glass plate, the joint between the two being made airtight with a little tallow. The cylinder is covered with a strong glass plate containing five or six holes, into which funnels are fitted by means of rubber stoppers. About 1 cm. below the rim of the cylinder are two tubes; to one is fitted the rubber tube from the pump, while the other contains a rubber stopper through which a testing spoon projects. By turning the funnel plate, any particular funnel can be brought over the testing spoon, and tests thus made during filtration. A vessel, *c*, standing on a thin felt board in the cylinder, serves to receive the liquid. This arrangement is preferable to a glass cylinder closed at the bottom, as it is thus possible to deal with hot liquids without danger to the apparatus.

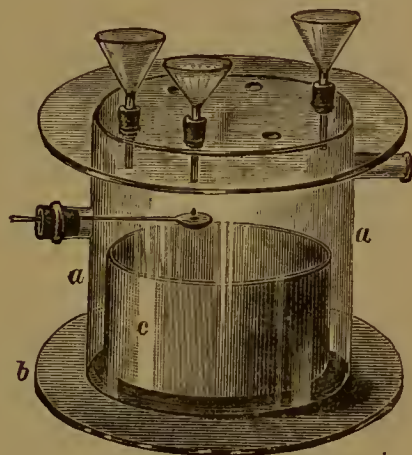


FIG. 97.

It is next necessary to take samples of both the ground and levigated products, to examine these for shade and body, and from the results to regulate the duration of the "wet grinding" and levigation. The quality of the colours depends on the fineness and uniformity of their grain. Grinding alone cannot completely bring about this condition, and a uniform degree of fineness can only be attained by a systematic method of levigation. This process is best carried out in five, six, or more wooden tanks in which the liquid remains undisturbed for a longer or shorter time, according to the degree of "darkness" of the quality aimed at, before being run off into the next tank. With regard to the tanks themselves care must be taken to have the first lot deep and narrow, and the lower ones wider and more shallow, as the darker particles, being coarser and specifically heavier, sink to the bottom more quickly than those that are lighter and paler, and for the latter the time of settlement will consequently be greater in deep tanks than in shallow ones. The result is that one and the same liquid, when allowed to remain undisturbed for the same length of time, gives a much darker levigation product in deep tanks

¹ This apparatus is supplied by the Vereinigte Fabriken für Laboratoriums-Bedarf, Berlin.

than in shallow ones. The whole process can be carried out much more quickly by means of a centrifugal machine.

The very finely divided particles remaining in the water are then precipitated by certain substances, and pressed in filter presses. Substances which simply precipitate the ultramarine mechanically are to be distinguished from those which exercise chemical action and coagulate the particles.

Supervision is also necessary, to a certain extent, in drying the ultramarine mud, for, as long as free sulphur is present in the ultramarine, shades totally different from one another may be obtained by drying the same quality at different temperatures. Drying with superheated steam can be strongly recommended, as most striking shades are thereby obtained.

III. THE EXAMINATION OF THE FINISHED ULTRAMARINE.

1. Colouring Power.—One-tenth gram of the sample is intimately mixed in a mortar, without using too much pressure, with 1 g. of very finely sieved burnt clay, or some other white powder. The mixture is then spread out on paper with a horn spatula and compared with a standard mixture or the mixture of another quality. An important condition for this test is good, bright but not dazzling light. Long practice is naturally required for the detection of slight differences.

It is advisable in this connection to make up, with a quality high in colouring power, a fairly large test in the same proportions—*e.g.*, 10 g. white and 1 g. blue, calling this mixture 50 per cent. A scale can then be drawn up, ascending with decrease of 0.5 g. white, and descending with increase of 0.5 g. white for each degree. These tests are labelled 51, 52, 53 per cent., etc., and 49, 48, 47 per cent., etc.

Other qualities mixed in the above proportions, viz., 0.1 blue : 1.0 white (always with the same white), are then compared with these standard tests. One quality may then be said to be of 54 per cent., another quality of 40 per cent. colouring power.

The Tint can also be examined by means of the spectroscope.¹ For this purpose the samples are mixed with a transparent varnish (rosin and turpentine varnish), and spread in this form on glass plates. After drying, the absorption spectra are determined.

2. Fineness.—An ultramarine of strong colouring power is of course at the same time extremely fine, but the finest quality is not always of high colouring power. Fineness is tested either by rubbing a small portion with the finger over a sieve of the finest silk gauze (about 160 meshes to the inch), when any coarse particles are easily felt, or 1 g. of the sample is weighed out and shaken in a bottle with 200 c.c. of water and then allowed to settle. The finer the blue, the longer will the water

¹ Cf. J. Wunder, *Ber.*, 1876, 9, 295.

remain coloured. This last operation also serves to test the "solubility"—that is to say, the miscibility of the ultramarine with water. Ultramarines which do not completely mix with the water when thus treated, but remain agglomerated, are useless for many technical purposes. The agglomeration of such qualities of ultramarine is mainly due to the use of an unsuitable precipitating agent, or to the presence of too much sodium sulphate in the wet ultramarine when the water is being driven off by evaporation.

It should, however, be noted, in connection with this test, that if ultramarine which is quite uniformly ground (so-called "amorphous ground") is well dried and then stirred up in water, it will no longer remain in suspension, but immediately settles to the bottom. This condition is a very important criterion, especially for colours used in lithography.

3. Examination for free Sulphur.—1 g. of the substance is slowly heated in a small glass tube sealed at one end. Ultramarine of good quality should only give a slight deposit of sulphur on the cooler parts of the tube. If the deposit is considerable, the ultramarine must be carefully heated at a moderately high temperature, or "desulphurised." Ultramarine for use in copper-plate printing and similar processes, even when moistened and rubbed on a bright copper plate and allowed to dry, should cause at the very most only slight tarnishing, if any.

4. Examination for Alum Resistance.—This chiefly concerns those qualities which are to be used for colouring paper. Fineness of grain is favourable to the decomposition. For the examination, 100 g. of alum are dissolved in a litre of water, the solution filtered, and 0.1 g. of the ultramarine to be tested treated in a test tube with 10 c.c. of the alum solution, the mixture well shaken at frequent intervals, and the decomposition observed. The longer the sample withstands decomposition, the better is the quality. This test is rendered more exact if 0.5 g. of the substance and 30 c.c. of solution are mixed together and allowed to stand for from two to three hours. The colour is filtered off, washed, dried, and then compared with the original by spreading out the two samples side by side.

The following test, though more troublesome, is very comprehensive. A thin pulp is made from filter paper, and a weighed quantity mixed with definite amounts of the sample of ultramarine and of the alum solution. The mixture is well stirred, filtered through a brass sieve by the aid of the pump, the small fragments of paper thus obtained dried, and then compared with those from a similar test of the standard quality.

5. Examination for use in Calico Printing.—Besides the examination for fineness, which is in this case very important, and which is carried out as described above, it is necessary, when ultramarine is

employed for calico printing, to investigate its behaviour towards the thickening medium with which it is mixed. The medium usually employed is albumin. Ultramarine favours the decomposition of albumin, but the rate at which it does so depends on the manner in which it has been prepared. The quality of ultramarine which shows the least tendency to cause putrid fermentation of the albumin is in this case the most serviceable.

The examination is carried out as follows:—To 2 g. of the sample, placed in a test tube on a foot, 2 g. of albumin and 10 c.c. of warm water are added. The mixture is thoroughly stirred and then allowed to stand for about twenty-four hours at a temperature of 25°-30°. The sample which best preserves the albumin and causes the least evolution of sulphuretted hydrogen is the best for the purpose.

6. Examination for use as a Lacquer.—1 g. of the sample is mixed with a few drops of the best linseed oil varnish on a glass plate, the mixture is allowed to dry, and is then examined in transmitted light. By this means the warm-coloured serviceable qualities can be distinguished with ease from the dull varieties.

IV. ANALYSIS OF ULTRAMARINE.

The works' analysis of ultramarine is confined to the estimation of free and chemically combined silica, alumina, sodium (Na_2O), and total sulphur.

1. Preparation of the raw Ultramarine for Analysis.—The colour is finely powdered and passed through a silk gauze sieve, after which it is dried at 100° for about twenty-four hours. From 2-10 g. are then weighed out and extracted with water, the solution made up to 500 c.c., filtered, and 100 c.c. taken for each of the following determinations:—

1. $\text{Na}_2\text{S}_2\text{O}_3$. By titration with iodine solution and starch; the result is expressed as $\text{Na}_2\text{S}_2\text{O}_3 + \text{aq}$.

2. Na_2SO_4 . By precipitation with barium chloride in acid solution.

3. NaCl . By precipitation with silver nitrate. (Sodium chloride is very seldom present in raw ultramarine.)

From 10-20 g. of ultramarine are partially washed by decantation two or three times successively, a quantity of alcohol being added in order to ensure a clear filtrate. The residue is treated with a dilute solution of sodium sulphite and the mixture evaporated nearly to dryness on the water-bath; this is done in order to remove free sulphur, as carbon bisulphide will only extract 40-60 per cent. of the latter. The residue is then washed until a dried portion of the ultramarine, when moistened with a little water and filtered, gives no trace of turbidity with barium chloride in the filtrate. This last operation

is very important, as otherwise the drying at a later stage cannot be effected without change occurring in the composition of the ultramarine. If the ultramarine is washed completely free from soluble salts, the blue, red, and yellow varieties may be dried at 100° - 140° or even at 150° without the slightest change taking place.

After being again finely powdered and dried at 130° - 140° , the ultramarine is transferred, while still hot, to a bottle fitted with a ground glass stopper.

2. Estimation of Silica, Clay Residue, and Total Sulphur.—1 g. of the dry substance is weighed into a porcelain dish, agitated as carefully as possible with water, and treated with 1-2 c.c. of bromine. Unless this operation is carried out with extreme care, small lumps are formed which are only decomposed on the outer surface, while inside the ultramarine is scarcely attacked at all. If the bromine is partially dissolved, which may be detected by the yellow colour of the liquid, 15-20 c.c. of nitric acid are added and the liquid evaporated to dryness on the water-bath. The residue is then taken up with water, about 20 c.c. of hydrochloric acid added, the solution again evaporated, the residue treated with hydrochloric acid, the mixture allowed to stand for some time (in the cold for twelve hours, hot for three hours), diluted with water, and filtered. The silica and clay residue (sand) remain on the filter paper, and are separated from one another as in the analysis of clay. The total sulphur is determined by heating the filtrate to boiling and precipitating with barium chloride. If the amount of iron in the ultramarine be considerable, which is seldom the case, the filtrate from the barium sulphate is reduced with zinc and titrated with permanganate solution.

3. Estimation of Alumina and Sodium Oxide (Na_2O).—1 g. of ultramarine, washed and dried as described above, is, as before, very carefully agitated with water and treated with excess of hydrochloric acid. After standing for some time, with occasional stirring, the mixture is heated until the solution becomes clear on allowing it to settle. The solution is then filtered off, when the sulphur, clay residue, and some silica remain as an insoluble residue; this residue is ignited and weighed. The filtrate is evaporated to dryness, the residue moistened with water and hydrochloric acid, again dried, then treated with hydrochloric acid, and the solution, after standing for a short time, diluted with water and filtered. Silica remains on the filter paper, and, when added to the residue obtained in the first filtration gives the amount of total silica and clay residue, which serves as a useful control of the determination described under (2).

The filtrate is evaporated to dryness to remove the excess of hydrochloric acid, the residue dissolved in water, precipitated with ammonia, and the whole again taken down completely to dryness on the water-

bath. By this means the alumina is obtained in such a condition that it can be easily and completely washed. The residue is taken up with hot water, the solution treated with a few drops of ammonia, heated, and filtered; the alumina remaining on the filter paper is ignited and weighed. Sodium (Na_2O) is determined by treating the filtrate with sulphuric acid and fuming nitric acid, and evaporating to dryness; by this treatment the creeping of the salts up the sides of the dish does not take place. The residue is very strongly ignited, and the amount of sodium as Na_2O calculated from the weight of sodium sulphate obtained.

4. Examination for Additions insoluble in Acid.—The following method devised by E. R. Andrews¹ has been designed to facilitate the examination of the pigment with regard to the possible presence of foreign additions insoluble in acid, an operation not easily performed when the sample is analysed by decomposition with acid. The process depends on the oxidising action of bromine and the subsequent complete solution of the products when the pure pigment is thus treated. 1 g. of the ultramarine is placed in a wide-mouthed flask of 150 c.c. capacity, and thoroughly wetted with 5-10 c.c. of water; about 30 c.c. of an aqueous saturated solution of bromine are then added, and the contents of the flask agitated until the colour of the bromine begins to disappear. More bromine water is added gradually until the blue colour of the ultramarine disappears and an excess of bromine remains. The flask is set aside for fifteen minutes, and the contents are then filtered quickly. The residue is washed with water, ignited, and weighed. The filtrate is acidified with 10 c.c. of strong hydrochloric acid, evaporated to dryness, the residue extracted with water, the silica filtered off, and the filtrate made up to a known volume. Aliquot portions of this solution are taken for determining the alumina, sulphur, etc. The weighed residue is boiled with sodium carbonate, filtered, washed, and re-weighed, the loss in weight being due to the invariable presence of a little silica in the insoluble residue. The amount of silica thus found (usually about 1.5 per cent.) is added to the bulk of the silica in the main filtrate. The matter insoluble in bromine water is stated to vary from 2.4-4.4 per cent. and to consist mainly of clay.

Note.—The statement found in many text-books, that sodium sulphide is a constituent of ultramarine, is not to be taken in the sense that this compound is present in the free state, but that its constituents are united with other elements, probably with aluminium, to form a complex product. This assumption explains the insensitiveness of the ultramarines towards white lead and other lead colours.²

¹ *Analyst*, 1910, 35, 157.

² Cf. A. Eibner, "Ueber Ultramarine," *Techn. Mitt. f. Malerei*, 1907, 23, 270.

Properties of technical Importance in Painting.—Blue ultramarines are unstable towards sulphur dioxide. They are frequently looked upon as absolutely fast to light and air, but this view does not appear to be correct in every case. Moreover, according to A. W. Keim, they are not all fast to lime. In fresco paintings, lime which is rich in silica destroys them in a comparatively short time, with the formation of discolouring, or colourless compounds. It is very probable that this change is aided by moisture, which also appears to play some part in the so-called "ultramarine disease." According to Pettenkofer,¹ this "disease" also occurs with the green earths (and with those pigments in general which are rich in clay, and therefore able to condense a large amount of water on their surfaces) in oil paintings subjected to great variations in temperature and moisture. He attributes the "disease" in such oil paintings to the fact that the "disease" of the colour itself, wherever it occurs in the painting, causes the vehicle (oil, etc.) to be more easily affected by moisture and changes of temperature, thus allowing the pigments to be visible through the cloudy medium of the disintegrated oil-layer. In contrast to this view Rohland traces the "ultramarine disease" to the superficial decomposition of the pigment by hydrolysis. E. Täuber has recently called attention to the relative lack of fastness to light of the violet ultramarines.²

Behaviour of Ultramarines in Mixtures.—Incorrect statements repeatedly occur to the effect that ultramarines, since they are sulphur colours, must react with lead pigments. These assertions are based partly on correctly made observations but wrong inferences, and also originate (like those made regarding mixtures of vermilion and white lead) owing to the technical impurity of one of the components, in this case the white lead. A. Eibner obtained the following results:—(1) Pure blue ultramarine, when boiled with a solution of lead acetate, is very strongly discoloured to blackish-blue; on the other hand, when boiled with pure white lead for the same length of time it remains unchanged. The discoloration is therefore caused by the technical impurity (lead acetate) in white lead, as in the case of the vermilion white lead mixtures. (2) Mixtures of the pure pigments remained unchanged during four years, and mixtures of the colours in oil during five years.³

Fastness to Zinc White.—A. Eibner found that the blue, as well as the green, violet, and red ultramarines, when made up into pale mixtures with zinc white and exposed in the form of water colours under glass to direct sunlight, faded distinctly within four months.

¹ "Ueber Oelfarbe," 1902.

² *Farben-Zeit.*, 1910, 15, 1382.

³ Cf. A. Eibner, *Malmaterialienkunde*, p. 180.

VII. VIOLET PIGMENTS.

Cobalt Violet.

By mixing solutions of cobalt sulphate and sodium phosphate, a rose-red precipitate of hydrated cobaltous phosphate is formed, which, on fusing, loses water, and in consequence assumes a violet colour. The melt is broken up, ground, washed, and dried, and then forms the dark cobalt violet of commerce. This pigment is semi-glazing, and permanent in mixtures with other mineral pigments. It is stated, however, that in practical use as a tempera or water colour it undergoes change of tone owing to gradual absorption of water. It appears to be quite fast to light. Washes prepared with gum arabic and with oil remained completely unchanged during seven years. Cobalt violet is also very stable towards zinc white. 12 per cent. mixtures in the form of water colours, exposed under glass to light, remained quite unchanged during two months.

A pigment differing from this form of cobalt violet is the cobaltous arsenite prepared by Gentele, which is a delicate red-violet powder, similar in shade and composition to the mineral, "cobalt bloom." It comes on the market under the name "Pale Cobalt violet," and is easily distinguished from the product described above by the odour of arsenic which is given off when it is heated on charcoal. This pigment is also very resistant towards zinc white. 12 per cent. mixtures in the form of water colours, spread out under glass and exposed to light, showed no change in two months (October to December).

Manganese Violet, Mineral Violet.

According to Mierzinski, this colour is prepared by fusing in enamelled cast-iron vessels a mixture of phosphoric acid and either finely powdered pyrolusite or the residues from the preparation of chlorine. The mass thus obtained is allowed to cool, and is then heated up to boiling with ammonia or ammonium carbonate solution, when manganese dioxide precipitates out. The liquid is filtered off, evaporated to dryness, and the residue heated until it melts; it is then allowed to cool, and boiled with water. A red liquid and a violet powder are obtained; the latter, after being washed and dried, constitutes the "Manganese violet."

A few years ago the firm of A. Behringer, of Charlottenburg, placed on the market a violet pigment in two shades, under the name "Mineral violet," which contained manganese, phosphoric acid, and ammonia. When heated alone it gives off ammonia, becoming white. It is decomposed by potassium hydroxide at ordinary temperatures, and by ammonia on warming, with separation of manganese dioxide, and

therefore appears to consist of manganous ammonium phosphate. Hence this pigment is related to, or identical with manganese violet. Its reactions suggest that it would not be fast to lime. As a matter of fact, however, it proved to be extremely stable when warmed with either calcium or barium hydroxide.

The pigment is analysed by decomposing it with excess of potassium hydroxide in a retort fitted with a condenser and receiver. The ammonia is determined volumetrically, and the manganese dioxide which separates out is dried and estimated iodimetrically. The phosphoric acid in the filtrate is precipitated with magnesia mixture, and weighed as magnesium pyrophosphate.

Mineral violet is very fast to light. Washes in gum arabic remained unchanged during four years.

Violet and Red Ultramarine.—These colours are obtained from blue ultramine by the action of dry hydrochloric acid and oxygen at 150° - 180° , whereby sodium is removed. Violet ultramarine, according to R. Hoffmann, is not an individual compound, but a mixture of blue and red ultramarine. It is manufactured from the blue variety by heating with ammonium chloride, and is then converted into the red form by means of hydrochloric acid. These colours have not, up to the present, acquired any great importance in commerce or in industrial applications.

VIII. GREEN PIGMENTS.

(a) Natural Products.

Green Earths (Seladonite).

(Bohemian or Veronese Earth; Tyrolean Green; Seladon Green;
Cyprian Earth; Terre Verte; Stone Green.)

The green earths are disintegration products of certain older minerals, chiefly of the hornblende series. In the crude state they form moist clay-like masses in a very fine state of division, which are improved by dry, or, more rarely, by wet dressing processes. They are characterised by their very fine grain, and, therefore, good spreading power and suitability for colour printing. Inferior qualities are used chiefly for industrial painting and as material for grounds in the manufacture of wallpapers, etc.; the finest qualities are employed for decorative and artistic painting. Formerly a mixture of ground green earth and white clay, under the name of "Stone green," was used for the manufacture of weather-proof paints.

The green earths differ essentially from the clays and chlorites in their small content of alumina, and from the chlorites also in containing

relatively small quantities of magnesia. Since they nearly always contain potash and soda, they belong to the hornblende group, and not to the augites. For a long time the colouring principle was assumed to be a ferrous silicate. According to Delesse,¹ a Veronese green earth contained :—

Silica	51 per cent.
Alumina	7 „ „
Ferrous oxide	21 „ „
Magnesia	6 „ „
Potassium oxide	6 „ „
Sodium oxide	2 „ „
Water	about 7 „ „

According to Church,² the iron in the green earths is present as ferric silicate.

The following figures are given for a product from Monte Baldo :—

Water, volatile at 100°	4.1 per cent.
Water, volatile at red heat	4.2 „ „
Ferric oxide (Fe ₂ O ₃)	20.3 „ „
Ferrous oxide (FeO)	2.6 „ „
Alumina	1.7 „ „
Lime	1.1 „ „
Magnesia	5.6 „ „
Potassium oxide	6.4 „ „
Sodium oxide	2.3 „ „
Silica	51.7 „ „

Gentile³ gives the following two analyses of Bohemian and English green earths respectively, the former containing ferrous, and the latter ferric oxide :—

Green earths.	Bohemian.	English.
Silica	41.0	56.4
Alumina	3.0	2.1
Ferrous oxide	23.0	5.1
Ferric oxide	14.1
Calcium oxide	8.0	...
Magnesium oxide	2.0	5.9
Potassium oxide	3.0	8.8
Carbon dioxide	19.0	...
Water	8.8

Analysis.—The contradictory statements regarding the degree of oxidation in which iron is present in the green earths seem to arise from the fact that even these pigments are still frequently looked upon

¹ Naumann, *Mineralogie*, p. 503.

² *The Chemistry of Paints and Painting*, p. 190.

³ *Lehrbuch der Farbenfabrikation*, vol. i., p. 153.

as individual substances, whereas they really appear to form a group of differently constituted isomorphous mixtures. The variety of their colour is, also, probably due to the varying content of ferrous and ferric iron respectively. Most of the green earths are not decomposed by hot hydrochloric acid, which only dissolves the ferric oxide formed by disintegration. The more valuable qualities of this mineral are by this means improved in tone, for on treatment with hydrochloric acid they lose their brown tint. According to Naumann,¹ green earths also exist which can be decomposed by hydrochloric acid. A Veronese green earth, decomposed by a mixture of hydrofluoric and concentrated sulphuric acid, gave a copious blue precipitate with potassium ferricyanide, and only a blue coloration with potassium ferrocyanide. In the ordinary method of silicate analysis by fusion with a mixture of sodium and potassium carbonates, all ferrous iron present becomes oxidised. Hence the ferrous iron present in green earths can only be estimated by decomposing with hydrofluoric acid, care being taken to prevent oxidation. This operation is carried out after the ferric oxide, formed by the disintegration of the earth, has been first removed by extraction with hot hydrochloric acid, and estimated. A further portion is then decomposed, and the total iron present is oxidised and estimated.

On ignition the green earths lose water, the iron becomes oxidised, and the resulting products are the "calcined green earths," which are fawn in colour, and are, likewise, used as painters' colours.

Lime Greens.—This designation applied originally to the green copper pigments imitating natural malachite, which are stable in lime. For the last twenty years the name has been understood to apply to particular kinds of German green earths, and to grey or white clays which have been coloured deep green by means of triphenylmethane pigments (malachite green, brilliant green). These substances are acid silicates, and exhibit the property of uniting in a particularly intimate manner with the basic pigments referred to. For this purpose the Rhenish, Hessian, and Saxon green earths, including the "Haiger earth," are especially suitable. The union of these coal-tar pigments with the earths is of interest from the theoretical as well as from the technical point of view. These acid clays are some of the few media available at the present day, by means of which very considerable fastness to light can be imparted to coal-tar pigments which are comparatively highly fugitive. When malachite green and brilliant green, unlaked and also as tannin lakes, are made up into washes with gum arabic and exposed to direct summer sunlight, they are completely destroyed within five days; but if precipitated on to green earths suitable for the purpose, they furnish lime greens in which the typical lack

¹ *Loc. cit.*

of permanence to light of the organic pigments is practically stopped. Four such lime greens, after exposure to direct sunlight for four years and seven months, had altered in tone only to the extent of assuming the well-known grey tint. There can be no doubt that pigments of this kind fulfil practical requirements for industrial painting and also as wallpaper colours. A corresponding improvement is observed in the behaviour of the four lime greens referred to above, in mixtures with zinc white. 4 per cent. mixtures of these pigments, made up into washes with gum arabic and exposed under glass to direct sunlight, suffered scarcely any diminution of their original intensity within two months. Thus, as regards fastness to zinc white, these lime greens are vastly superior to the Prussian blues, chrome greens, zinc greens, etc., and in this respect are about equal to the ultramarines. On the other hand, the colour of a different lime green had completely disappeared in four years, the illuminated half of the test card taking on a reddish-grey shade. The same lime green, in 4 per cent. mixture with zinc white, faded in two months into reddish grey-green, and decreased considerably in intensity.

It is well known that all green earths, grey clays, plastic white clays, boles, etc., do not render basic coal-tar pigments such as malachite green, brilliant greens, auramine, etc., equally fast to light. A particularly noteworthy property of the Rhenish, Hessian, and Saxon grey earths is their capacity for rendering these basic pigments non-sensitive even towards alkalis. G. Zerr¹ states that the colour lakes in question have, at first, a dull dark olive-green appearance, and when dry look almost black. If, however, they are treated with dilute sodium hydroxide solution, instead of the decolorisation such as the free malachite and brilliant greens, etc., undergo, the bluish-green and vivid coloration peculiar to the lime greens appears, generally at once, and undergoes no alteration on further treatment. It would seem, therefore, that during the formation of these lime greens alkali enters into the union of pigment and substratum. From their behaviour towards alkali a trustworthy conclusion as to their fastness to lime may be drawn.

With a decrease in the acid character of the grey earths employed, the fastness of the lime greens to light and to lime decreases. The best of the lime greens mentioned are also fast to water and spirit.

The mineral *Malachite* was formerly mined under the name of "mountain green," especially in the Tyrol, for the purpose of working it up into an industrial and artists' paint. Nowadays this pigment is only found occasionally amongst artists' colours. Nearly all the modern "mountain greens" of commerce are artificial copper pigments (see p. 1006).

¹ *Farben-Zeit.*, 1911, 16, 14, 70, 544.

(b) Artificial Green Pigments.**Cobalt Green (Rinmann's Green).**

This pigment is prepared, as in the case of cobalt blue, either by starting from soluble cobalt salts, treating them with sodium carbonate, mixing the precipitate with zinc oxide in suitable proportion, drying, and igniting; or else by preparing cobalt phosphate or arsenate, and treating it in a similar manner. The latter method is said to give warmer colours than the former, and to allow of the colour being produced at a lower temperature. If for one equivalent of zinc oxide more than one equivalent of cobaltous oxide is used, a dirty green colour results. Good colours are said to be obtained if for 9-10 parts by weight of zinc oxide $1-1\frac{1}{2}$ parts of cobaltous oxide are employed.¹ Hence it follows that the cobalt greens, like the cobalt blues, do not consist of one individual chemical substance, and cannot be regarded as pure cobalt zincate. The cobalt greens are put on to the market in three degrees of shade, namely, "light," "medium," and "dark," which differ also in tint, varying from bluish- to yellowish-green. Like cobalt blue they can be looked upon as substratum colours, in this case containing more or less zinc oxide. The mean percentage composition is stated to be 88 per cent. zinc oxide and 12 per cent. cobaltous oxide. According to Wagner a dark cobalt green contained 71.93 per cent. zinc oxide, 19.15 per cent. cobaltous oxide, 8.23 per cent. phosphoric acid, and 0.69 per cent. sodium oxide.

Analysis.—Cobalt greens dissolve when heated with hydrochloric acid, giving a red solution. On continued boiling with the darker varieties, potassium hydroxide is coloured light blue, and ammonium carbonate solution a very beautiful violet. Phosphoric acid appears to occur only rarely in the cobalt greens manufactured at the present day. Out of twelve samples examined it was present in only one. For quantitative analysis the cobalt greens are dissolved in nitric acid. Cobalt is precipitated as potassium cobalti-nitrite, the precipitate washed, dissolved in hydrochloric acid, and hydrated cobaltous oxide then precipitated and determined as metal by Rose's method. Nickel, if present, is precipitated from the filtrate, after boiling with excess of hydrochloric acid, by means of potassium hydroxide, and is converted into nickelous oxide. Zinc is precipitated from the filtrate as sulphide, and, after ignition, determined as oxide.

Fastness to Light and Compatibility in Mixtures.—The cobalt greens are permanent in the light. They are unstable in mixtures with zinc yellow, yellow ultramarine, or zinc green. Towards zinc white, cobalt green proved to be much more stable than the ultramarines; 10 per cent. mixtures in the form of water colours exposed to light under

¹ Cf. Munkert, *Normalfarben*, p. 151.

glass underwent practically no change in two months. This behaviour is explained by the fact that the cobalt greens possess to some extent the composition of zincates.

Gellert Green is a variety of cobalt green, and is obtained by roasting and igniting metallic cobalt with 4-5 parts of saltpetre and 8-10 parts of zinc oxide.

On account of their relatively high cost these pigments are chiefly used as artists' colours.

Manganese Green.

(Cassel Green; Rosenstiel's Green; Baryta Green.)

This pigment, which is but little used, and is said to be sensitive to moisture, is obtained by heating a mixture of oxides of manganese, barium nitrate and heavy spar, or kaolin. Barium peroxide is also used.

The Green Chromium Pigments.

The trade name "chrome green" was formerly applied to chromium sesquioxide, Cr_2O_3 , or to the green colours closely related to it. Later, however, the name was also applied to the cheaper green mixtures prepared from chrome yellow and Prussian blue, from which the true chrome green is now distinguished by the name "chrome oxide green."

Chrome Oxide Green (Dull or non-glazing).

The technical methods of preparing "dull chrome oxide green" depend on the reduction of chromates by the use of suitable reducing agents, and aim at producing a pigment of the highest possible brilliance and suitability for colouring purposes. Like the varieties of mercuric oxide, cadmium yellow, and the red iron colours, chromic oxide exhibits marked differences in density and size of grain and, therefore, in shade, according to the method of preparation, temperature, nature of additions, etc., used in its manufacture. According to Dieterich, sulphur, soft wood-charcoal, potato starch, and paper-makers' wood-pulp serve as reducing agents; while Casali states that gypsum and picric acid are also used. The products of these various methods of preparation exhibit considerable differences in tone. The colour obtained from mercurous chromate is the most beautiful, but it is too expensive. Approaching the latter is the colour obtained by means of picric acid, whilst that produced with sulphur is duller.¹ On the other hand, the green product which results from the decomposition of ammonium bichromate on heating, is not the oxide Cr_2O_3 , as is generally stated, but a mixture of the latter with the dark brown chromium dioxide CrO_2 .

¹ For details of the manufacture, see Zerr and Rübencamp, *Colour Manufacture*, p. 231.

Analysis.—Chrome oxide green, prepared in one or other of the above ways, is usually almost chemically pure chromic oxide, Cr_2O_3 , as the by-products formed during the manufacture are easily removable by water or acids. Adulterants are scarcely ever present. Its shade alone serves to distinguish it from the green vermilions, green earths, etc.; it differs also from the latter in its stability on ignition and on warming with alkalis. The valuation is carried out by fusing with potassium nitrate and sodium carbonate, dissolving the melt, and separating the alumina and iron. After reducing by means of alcohol and hydrochloric acid, the silica is separated by evaporating to dryness three times, and the chromium precipitated in the filtrate as hydroxide, ignited, and weighed as Cr_2O_3 .

“Dull” chrome oxide green was formerly used more especially for glass and porcelain painting, also for printing bank-notes, as it cannot be reproduced by photographic processes; a further use was for printing wallpaper. For a long time past the consumption of this colour has largely diminished, owing to its comparative dearness and lack of brilliance. It is still used, however, to a large extent as an artists' colour. It is a pronounced body colour, and is stable in mixtures with other pigments.

Guignet's Green.

(Emerald Green; Chrome Green; Vert de Guinet; Victoria Green.)

Guignet's green is made by heating a mixture of 1 part of potassium or sodium bichromate and 3 parts of crystallised boric acid in a muffle at about 700° . Reduction of the chromate takes place with the formation of chromium metaborate together with alkali borate. The former, on further heating, is converted into an alkali-chromium pyroborate which is dark green in colour and, on hydrolysis, gives Guignet's green. Besides this main reaction certain secondary reactions also occur.

Since all commercial samples of Guignet's green contain boric acid, Shipton¹ assumed that it was an integral component of the pigment, and gave the formula $\text{BO}_3 \cdot 3\text{Cr}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ to the pigment. On the other hand, Guignet and Salvétat recognised that the boric acid was a technical impurity, and put forward the formula $\text{Cr}_2\text{O}(\text{OH})_4$, which requires 19.1 per cent. of water. Scheurer-Kestner subsequently found about 15 per cent. of water, corresponding to the formula $\text{Cr}_4\text{O}_3(\text{OH})_6$. L. Wöhler and W. Becker² have recently confirmed this formula for the commercial Guignet's greens. On the other hand, they obtained from ammonium bichromate greens with a maximum water-content of 37 per

¹ *Dingl. polyt. J.*, 1865, 176, 315.

² *Z. angew. Chem.*, 1908, 21, 1600; *J. Soc. Chem. Ind.*, 1908, 27, 865.

cent. Wöhler then prepared a green, insoluble in hydrochloric acid and possessing the tone of Guignet's green, by heating precipitated chromium hydroxide with water under pressure, the product being free from all the secondary constituents and impurities present in the commercial Guignet's greens.

The investigations into the constitution, methods of formation and analysis of Guignet's greens, begun in 1908 by A. Eibner and O. Hue, have given the following results:—The commercial products "pale" and "dark" Guignet's greens are not chemical individuals but mixtures of (1) Two chief constituents insoluble in acids, viz.—the hydrates $\text{Cr}_4\text{O}_3(\text{OH})_6$ and $\text{Cr}_4\text{O}(\text{OH})_{10}$, on which the characteristic shade depends, and the following secondary constituents present in small quantities: (2) Chromium sesquioxide, Cr_2O_3 , which is formed when the temperature exceeds 700° and the charge is in that way partly "overburnt." (3) The brownish-black chromium peroxide, Cr_3O_6 , which is chiefly formed when too little boric acid is present. (4) Alkali, occluded by the chromium hydroxide, and which is very difficult to remove. In addition, a fifth constituent, chromium metaborate, occurs in many samples of Guignet's green as an intermediate product; it is soluble in acids. Boric acid is to be looked upon as a technical impurity which on the large scale, cannot be completely removed; some of the newest brands showed only a small content of this component (6.82, 4.29, 1.95 per cent.). Some Guignet's greens contain, as further technical impurities, small quantities of alkali chromates and iron compounds. In the case of commercial greens prepared from alkali bichromates the content of water varies between 15 and 22 per cent., and in those from ammonium bichromate, between 25 and 43 per cent.; a portion of the water is present in the adsorbed state. Guignet's greens are therefore hydrogels, like the Prussian blues. Under certain experimental conditions they pass into hydrosols (colloidal solutions of Guignet's green).

The greens prepared from ammonium bichromate, when made on the small scale, are free from Cr_2O_3 and Cr_3O_6 and, in consequence, possess a much higher glazing power than the commercial greens. Moreover they are free from alkali. The green which L. Wöhler¹ obtained by heating precipitated chromium hydroxide with water under pressure forms the purest and most highly glazing Guignet's green that exists. It corresponds most nearly, therefore, without regard to its character as a hydrogel, to the formula advanced by Scheurer-Kestner.²

¹ *Loc. cit.*

² For further researches on the composition of Guignet's green, see Eibner and Hue, *Farben-Zeit.*, 1910, 51, 2106, 2157, 2213, 2268, and 2319; also, L. Wöhler and W. Becker, *Z. angew. Chem.*, 1911, 24, 484; *J. Soc. Chem. Ind.*, 1911, 30, 559.

Analysis.—From the foregoing statements it is clear that the method of analysing Guignet's greens adopted up to the present, by fusing with sodium carbonate and potassium nitrate, does not lead to the determination of all the constituents. In the first place the adsorbed water should be estimated by determining the loss of weight on standing in an exsiccator over sulphuric acid. Further, in estimating the total water-content it must be borne in mind that chromium hydroxides, when heated in the air, are converted into peroxides, which only decompose into Cr_2O_3 and oxygen on the application of a very strong red heat. The substance must therefore be heated over the blowpipe until the black mass has become bright green. Before estimating the boric acid it is necessary to ascertain whether any portion is present in the combined state as chromium metaborate; this is done by extracting with hydrochloric acid. The boric acid content is determined by difference as follows:—After ignition, the green residue is weighed and is then treated with a mixture of hydrofluoric and sulphuric acids on the sand-bath, and the boron volatilised. After washing out the alkali, the boron-free oxide is then dried and weighed.

Potassium is estimated by heating the ignited sample with a mixture of hydrofluoric and sulphuric acids as described above, lixiviating the residue with water, and precipitating with ammonium hydroxide. The filtrate is evaporated and the residue heated until the ammonium salts are driven off; it is then taken up with sulphuric acid, and the potassium determined as sulphate. Up to the present time there is no method for the direct estimation of the Cr_2O_3 contained in the commercial Guignet's greens. It was found that these greens, when heated with concentrated sulphuric acid, were capable of being slowly converted into soluble sulphates; the oxide Cr_2O_3 would then probably remain as a residue. This method has still to be worked out. In the same way the estimation of the chromium peroxide is still uncertain. Since it can only be decomposed by hydrochloric acid with great difficulty, the iodometric method is scarcely applicable, and the peroxide must be estimated by measuring the oxygen evolved on heating the pigment in an indifferent gas.

Chromium Phosphate Greens.

Arnaudon's Green is prepared by stirring up 128 parts of ammonium phosphate and 149 parts of potassium bichromate with water to a paste, and heating the mixture to 170° - 180° , whereby reduction takes place; the temperature must not rise above 200° . The green mass obtained is lixiviated with water. The green produced in this way is not much inferior in beauty to Schweinfurth green. When heated in a tube

it does not, like Guignet's green, become black, but violet-red, and green again on cooling. This colour is probably a basic chromium phosphate.

Schnitzer's Green, which differs from the above as regards the mode of preparation in that crystallised sodium phosphate is used, is of similar composition.

Mathieu Plessy's Green is prepared by warming together 10 kg. of potassium bichromate dissolved in 10 kg. of boiling water, 3 litres of calcium phosphate solution containing 6.5 per cent. of phosphoric acid, and 5 kg. of sugar or starch-sugar as a reducing agent.

Ultramarine Green is the intermediate product of the indirect manufacture of blue soda-ultramarine, and the end-product of the raw-burning process in the production of sulphate-ultramarine. It does not possess the depth and brilliance of the blue ultramarines, and is also duller than the Permanent greens. It is, however, manufactured for use as a lime wash, for printing wallpaper, etc. Ultramarine green varies, according to the duration of burning and the temperature, from yellow-green to blue-green, and also in depth of shade. It differs from blue ultramarine, *inter alia*, in possessing a higher content of sodium.¹ (For analysis, see Ultramarine, p. 990.)

(c) Green Mixture-pigments of Chrome Yellow and Paris Blue.

Chrome Green.

(Green Vermilion; Printing Green; Milori Green;
Satin Green; Silk Green.)

These names are now quite generally understood to apply no longer to the green colours of which the basis is chromium oxide, but to the above mixture-colours. While the colours now designated by the name "zinc greens" (mixture-colours) are chiefly used in oil, the chrome greens serve more particularly as wallpaper and lithographic colours. When used for the former purpose they are called "printing greens"; in lithography "silk greens," "satin greens," and also "Milori greens." Silk greens contain blanc fixe as a substratum, which is always freshly prepared. The correct designation, and the one which has recently come into vogue to some extent, is "chrome-yellow greens." For the purpose of manufacturing cheap varieties and pale shades of these colours they are treated with varying quantities of heavy spar. According to the proportions of chrome yellow to Prussian blue, varieties are obtained with a blue and yellow cast respectively. The former occur under fancy names such as:—Oil green, maple green, leaf green, moss green, emerald green, etc.; the latter as:—May green,

¹ R. Hoffmann, *Ultramarin*, p. 88.

mignonette green, etc. These colours are prepared either in the dry way by mixing in edge runners, or, in order to obtain a more intimate mixture, by the wet process, in which the Prussian blue is first fixed on to the heavy spar and then used as the so-called "blue spar" (mineral blue) in the form of a paste. Chrome yellow in the form of lemon chrome yellow is used for the paler varieties of chrome green. The chrome greens, like their two components, are not fast to lime, and therefore cannot be employed as lime colours. Their permanence in light is limited by the content of chrome yellow. Chrome greens from ultramarine and copper colours are seldom made nowadays.

Zinc Greens.

The name "Zinc green" is now applied exclusively to mixtures of zinc yellow and Prussian blue, that is, "zinc-yellow greens." Like the chrome greens, they contain varying quantities of heavy spar or blanc fixe and are likewise prepared in many different shades, which are purer but also paler than the chrome greens. The palest varieties possessing a yellow tint are known as "parrot greens." (Varieties of Schweinfurth green also pass under this name.) The so-called "blueing" of zinc greens, when used as oil colours, occurs as a result of faulty preparation, and is caused by the Prussian blue making its way to the surface. The zinc greens are just as unstable towards lime as the chrome greens, but, on the other hand, are much faster to light.

Analysis.—Chrome greens and zinc greens are decomposed by potassium hydroxide. The former give chrome red and hydrated ferric oxide, which are found in the precipitate, and potassium-lead oxide and potassium ferrocyanide, which remain in the filtrate. The zinc yellow in the zinc green is completely dissolved by potassium hydroxide, so that in this case the precipitate only consists of heavy spar and hydrated ferric oxide, all the zinc, together with the potassium ferrocyanide, being in solution. Paler chrome greens are recognised by the reddish colour of the precipitate, due to the chrome red. In the case of the darker varieties it may be difficult to draw a distinction. In this case the filtrate is treated with ammonium sulphide; a black precipitate indicates the presence of chrome green, and a white precipitate that of zinc green.

The method of procedure in the quantitative analysis of chrome and zinc greens is regulated according to the constituent to be estimated.

Green Vermilion, English Green, Mineral Green.—These colours are closely related to the chrome greens, and are usually prepared by treating Prussian blue, rendered soluble by oxalic acid, with a solution

of potassium bichromate, and then adding a solution of lead acetate. If barium salts are used for precipitation, shades similar to the zinc greens are obtained.

According to G. Wendt, a green vermilion containing no yellow is prepared by adding 1 part of a solution of potassium ferrocyanide saturated in the cold to 15 parts of oxalic acid, and warming on the water-bath until the dark blue turbidity which forms at first has changed to a sea-green. This mixture is then poured into a solution of 15 parts of ferrous sulphate saturated in the cold. The name "green vermilion," being a spurious substance designation, should be abandoned.

Fastness to Zinc White of the chrome greens and zinc greens.—Since both Prussian blues and chrome yellows in the form of water colours are extraordinarily sensitive in sunlight towards zinc white, and zinc yellow under similar conditions is also unstable, it is to be expected that the chrome greens and zinc greens will exhibit the same defects. This is the case:—1 per cent. mixtures of chrome greens and zinc greens with zinc white faded considerably within a month, and at the same time assumed a strong blue tint. The yellow component is therefore more rapidly destroyed than the blue, a fact due to the reversibility of the light reaction in the latter case.

(d) The Green Copper Pigments.

1. *Imitation Native Malachite Greens.*

Mountain Green was formerly prepared by precipitating a boiling solution of alum and copper sulphate with a hot solution of sodium or potassium sulphate (Mierzinski). The Mountain green obtained according to Gurth's method contains added Schütt yellow. Varieties of mountain green blended with white clay, heavy spar, etc., are known under the names "Alexander green," "Glance green," and "Napoleon's green."

Lime Green (Earth Green).—This name was originally given to a pigment obtained by precipitating copper sulphate solution with chalk, or milk of lime. It is not stable.

Bremen Green is the intermediate product in the preparation of Bremen blue (p. 976).

Brunswick Green was originally obtained by treating copper sulphate with common salt, and precipitating with milk of lime; in this case it is a basic copper chloride. When precipitated with sodium carbonate it possesses the composition, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$. At the present day the name has been transferred to mixtures of chrome yellows and blue, to which the names "Prussian green" and "Victoria green" are also applied. The name "Brunswick green" is, however, also applied to

Bremen blue and to an arsenical copper green containing no acetic acid, as also to a variety of Schweinfurth green.

Erlau Green is prepared in a similar way to the old Brunswick green, by adding a mixture of copper sulphate and common salt to milk of lime, washing the precipitate obtained, and treating it with a solution of neutral potassium chromate. Vienna white or heavy spar is added to it.

Bolley's Green is a copper borate dehydrated by heating to redness. It possesses good covering power and is used as an oil colour. Little use is made of it at the present day.

Gentile's Green, tin-copper green, is obtained either by precipitating copper sulphate solution with stannous chloride and washing and drying the precipitate, which is white at first but later becomes green; or else by using sodium stannate and washing the precipitate (which is at first orange-yellow), whereby it gradually becomes green.

Elsner's Green is a mixture of tin-copper green and fustic decoction.

2. Verdigris.

These colours include the true verdigris (Verdit, Verdet, Grünspan), which occurs in two varieties: as "Neutral blue" or "Crystallised Verdigris," in the form of "grapes," and as "Basic Verdigris" in balls. At one time it was prepared by the action of wine residues on copper; acetic fermentation sets in and the immediate product is neutral copper acetate. At the present time vinegar is used, or calcium or sodium acetate is allowed to act on copper sulphate, or else copper carbonate is dissolved in vinegar. Crystallised verdigris approaches the composition, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, but it also contains basic acetate. The composition $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{Cu}(\text{OH})_2$ is ascribed to the basic green - coloured verdigris. Three kinds of verdigris, English, French, and German, are recognised. Verdigris should dissolve completely in ammonium hydroxide, or at any rate not leave more than 2-3 per cent. of residue. Additions of chalk, gypsum, and heavy spar are sometimes made. Verdigris is a glazing colour; it is very unstable, and its consumption is decreasing.

Casselmann's Green is a basic verdigris obtained by mixing a boiling solution of sodium acetate with copper sulphate. Next to Schweinfurth green it is the most beautiful copper colour. It has the composition $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$.

The so-called *Saxon Verdigris* approaches Brunswick green in composition, and is formed by precipitating a mixture of copper sulphate and common salt with milk of lime. It contains gypsum or Vienna white.

3. *Arsenic Greens.*

These colours consist of either basic arsenite or arseno-acetate of copper, with or without additions. Included in the former class is *Scheele's Green*, which was originally prepared by treating a solution of copper sulphate with a solution of white arsenic in sodium carbonate, and then adding caustic soda solution until copper could no longer be detected in the filtrate from the green precipitate which was formed. This green varies in colour from canary-green to dark green, according to the amount of arsenious acid it contains.¹

Another pigment sold under the name of *Scheele's green* is obtained by precipitating a dilute solution of copper sulphate with an alkaline solution of arsenic. It has fairly good covering power, and can be used as a water and oil colour as well as for lime wash.

Emerald Green (usually called *Schweinfurth Green* in Germany).—Some fifty names have been employed for the designation of this green in its various pure and adulterated forms, and as prepared by the older or newer methods. Some of these indicate its origin, whilst others are fancy names, the object of which has been to disguise the poisonous character of the colour. The older names for emerald green are:—Mitis, Vienna, Paris, Verdigris green (for an emerald green prepared according to the old method, from verdigris), Emperor, New, Mineral, Original green, Vert Paul Veronese, etc. It occurs under the last name as an artists' colour.

The modern method of preparing emerald green consists, in the first place, in mixing a hot solution of white arsenic in sodium carbonate with the calculated quantity of copper sulphate solution. Dirty green copper arsenite is formed. After some time, the required quantity of acetic acid is added, with stirring, at a temperature of about 80°, and the solution is then diluted with water until the temperature has fallen to 20°. In about an hour the formation of the green, which takes place with evolution of carbon dioxide, is complete. The beauty of the shade depends on the manner in which crystal formation takes place. Emerald green is the most beautiful green inorganic colour known. The more arsenic it contains, the paler it is. It is a double salt of copper arsenite and copper acetate and has the formula, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{CuAs}_2\text{O}_4$.

Analysis.—Pure emerald green dissolves in ammonium hydroxide, leaving no residue. When heated with dehydrated sodium carbonate in a tube it evolves an odour of cacodyl.

Mineral admixtures are detected as follows:²—An effervescence on dissolving in acid indicates the presence of copper carbonate. An

¹ Cf. Zerr and Rübencamp, *Colour Manufacture*, p. 227.

² Cf. B. Stillmann, *Chem. News*, 1899, 80, 251.

insoluble residue remaining after this treatment may contain clay, heavy spar, and gypsum. A precipitate formed on treatment of the hydrochloric acid solution with excess of ammonium carbonate may contain aluminium, calcium, and magnesium. The presence of chrome yellow may be detected¹ by dissolving in hydrochloric acid (a white precipitate is often formed which disappears again on the addition of a large quantity of water), diluting with water, and adding sulphuric acid. The lead sulphate is filtered off, and the filtrate boiled, with addition of alcohol; on adding ammonium carbonate chromic hydroxide is precipitated out.

The amount of copper is estimated by dissolving the emerald green in hydrochloric acid, treating the solution with excess of ammonium carbonate, filtering off any precipitate formed (alumina, calcium, magnesium), and precipitating the copper in the boiling filtrate with sodium hydroxide.

The microscopic examination of the colour is also of importance. This is best carried out by mixing it with a drop of glycerin on a slide, without grinding, and laying a cover-glass over the mixture; the magnification required with dark greens is about 200, with lighter greens from 400-500. Heavy spar and light spar (naturally occurring ground gypsum) are easily recognised by this examination. The presence of octohedra of arsenious oxide (Fig. 98) indicates that the colour is a verdigris green, prepared by the verdigris method.²

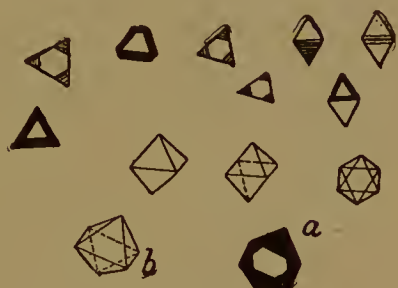


FIG. 98.

S. Avery and H. T. Beans³ have shown that the usual methods for estimating the soluble arsenic trioxide in emerald green, depending essentially upon extraction with water, are impracticable, and recommend the following procedure:—1 g. of the colour is heated for five minutes with 25 c.c. of sodium acetate solution (12.5 g. in 1000 c.c.); the solution is cooled, made up to 100 c.c., and an aliquot portion titrated with iodine solution.

J. K. Haywood⁴ has proposed a modification of Avery and Bean's method for the estimation of the total amount of arsenic trioxide. The latter method gives very good results if the samples of emerald green are pure, but if much free arsenious oxide is present the results are too low. The following method is therefore adopted:—2 g. of an average sample are powdered in an agate mortar, and 0.3-0.4 g. of the powder treated in a beaker with 25 c.c. of water; concentrated

¹ Bolley-Stahlschmidt, *Handbuch der techn. chem. Untersuchungen*, 1889, p. 352.

² Cf. *Z. angew. Chem.*, 1888, **1**, 47.

³ *J. Amer. Chem. Soc.*, 1901, **23**, 111.

⁴ *Ibid.*, 1903, **25**, 963.

hydrochloric acid is then added, drop by drop, with constant stirring, until the colour is all dissolved. Under these conditions free arsenious oxide remains insoluble and is filtered off and washed; the arsenious oxide in the filtrate is estimated by Avery and Bean's method. The filter paper and its contents are washed out of the funnel into a beaker, treated with 5 g. of sodium bicarbonate, boiled for five to ten minutes until the arsenious oxide is completely dissolved, the solution cooled, acidified in presence of a drop of methyl orange, then rendered alkaline again with sodium bicarbonate, and after addition of starch solution, titrated with iodine solution.

In cases where free arsenious oxide is present, S. Avery¹ recommends the following treatment:—The sample is gently heated with about $N/2$ hydrochloric acid, using 5-10 c.c. for every 0.1 g.; if the substance does not dissolve completely, a cold saturated solution of sodium acetate (about 3 g. of the salt for every 0.1 g. of the sample) is added, and the mixture boiled until all the arsenious oxide is dissolved. All the copper must be in solution before the addition of the acetate. When the substance is completely dissolved, alkali tartrate and solid bicarbonate are added, and the dilute solution then titrated in the usual manner.

Analyses of Emerald Green.—Forty-four commercial samples examined by L. L. van Slyke and W. H. Andrews² in 1902, contained:—

Mean.			
55.39 to 61.40	=	57.10 per cent.	As ₂ O ₃
0.61 „ 1.35	=	1.01 „	As ₂ O ₃ , soluble in water
27.03 „ 30.79	=	29.41 „	CuO
50.63 „ 57.60	=	55.10 „	As ₂ O ₃ , combined with copper.

The arsenic greens known as *Soda greens* are obtained by neutralising with sodium carbonate the mother liquor containing white arsenic, acetic acid, and dissolved emerald green, which is produced in the preparation of the latter. If the neutralisation is carried out with milk of lime, the resulting products are the *Line-arsenic greens*.³

Neuwied Green is a mixture of emerald green with varying quantities of gypsum, heavy spar, or blanc fixe. It is prepared by a process similar to one of the old methods for obtaining emerald green. It is now only rarely found in commerce.

Compatibility in Mixtures.—As already mentioned, emerald green, in the presence of cadmium yellow, orange, and red, very rapidly undergoes double decomposition with the formation of copper sulphide. Partial discoloration of mixtures with ultramarine, Saturn red, and vermilion has been observed to take place within a year.

¹ *J. Amer. Chem. Soc.*, 1903, 25, 1096.

² *New York Agricultural Exp. Sta., Geneva, N.Y.*, Bull. No. 222, 1903, p. 265.

³ Zerr and Rübenkamp, *Colour Manufacture*, p. 219.

IX. BROWN PIGMENTS.

(a) Natural Products.

Umber, Umber Brown (Mineral Umber).

(Velvet Brown; Chestnut Brown; Manganese Velvet Brown;
Burnt Umber.)

The mineral varieties of umber are ochres coloured brown by oxides of manganese, and containing varying amounts of clay. The finest qualities are found in Sicily and Cyprus; they also occur at Saalfeld in Thuringia, in the Harz and Rhine districts, in Bavaria, etc. The designation "umber" has also been applied to brown earthy products which contain lignite as the chief component, and are therefore, for the most part, soluble in warm potassium hydroxide. The so-called "Cologne umber" (Cologne earth), coal brown, Cassel brown, etc., also belong to this class. Since the latter colours exhibit various defects such as solubility in oil, fading in the light and darkening, the name "umber" should be confined to the genuine mineral varieties of umber, which should contain no organic constituents.

Analysis.—Mineral umber, when heated, gives off water only and no combustible products; on warming with hydrochloric acid chlorine is evolved. Since the shade of these colours depends on the proportion of iron and manganese compounds present, the determination of the content of manganese is often necessary and is carried out iodometrically. The remainder of the analysis is identical with that of a silicate, including the estimation of water.

By calcining the raw product "Burnt Umber" is obtained. It possesses a deeper and more reddish tint than the native variety. The genuine mineral varieties of umber are used as paints and as wall-paper, printing and artists' colours. The "Fawns" are very pale varieties of umber containing little manganese; they are also manufactured by mixing native or burnt umber with dark ochres, to which they are closely related. Both fawns and umbers are frequently prepared artificially from ochres by the addition of charcoal black. These products are recognised by the absence of manganese and by the floating particles of charcoal which separate on washing. *Bronze browns* are mixtures of unburnt umber and chrome yellow, toned with Cassel brown, chrome orange, black pigments, green mineral colours or ferric oxide colours. The well-known *Vandyke browns* are produced in a similar way.¹

¹ Cf. Zerr and Rübencamp, *Colour Manufacture*, p. 400.

(b) Artificial Products.

Berlin Brown is produced by charring Prussian blue, and is a mixture of ferroso-ferric oxide, ferric oxide, and charcoal. It is only used as an artists' colour.

Florentine Brown, also known as Vandyke red and Hachette brown, is copper ferrocyanide. Its permanence in the light is not as great as that of the unmixed Prussian blues. As regards its compatibility with other pigments, sufficient data are not yet available.

X. BLACK PIGMENTS.**Graphite.**

(Stove Polish; Black Lead; Plumbago.)

Graphite occurs chiefly in the Ural Mountains of Southern Siberia, in Ceylon, in England and Scotland, in Sweden, Bohemia, Moravia, and Bavaria. The most costly variety, containing 1-6 per cent. of ash, is obtained from Ceylon. The less pure kinds contain from 40-60 per cent. of ash which consists chiefly of ferruginous sand and clay. Distinction is drawn between amorphous graphite (sp. gr. 1.8), which is used as a colour, and foliaceous graphite (sp. gr. 2.1-2.5) which, on account of its structure, is better able to withstand a high temperature, and is therefore used for the manufacture of crucibles. Ground graphite is of a darker shade than the levigated product. The latter is more of a silver-grey and exhibits a metallic lustre when spread out with a palette knife, on account of the separate leaflets coming into a parallel position and reflecting the light. Hence it is called "silver graphite." Practically the only use for graphite as a colour is for blackleading stove-pipes. For the manufacture of lead pencils the purest amorphous graphite is used, mixed with clay.

Analysis.—The valuation of graphite, according to M. Schwarz,¹ is carried out by mixing a weighed quantity with excess of lead oxide in a crucible. The vessel is well covered, the mixture heated up to the melting point of lead oxide, and after cooling, the weight of the lead regulus at the bottom of the crucible is determined: 207 parts of lead are reckoned as equivalent to 6 parts of pure graphite (or 34.5 parts to 1 part of carbon); this method is very exact.

Wittstein's method of analysis consists in heating 1 g. of finely powdered graphite to a dull red heat; the loss of weight is calculated as water. The dried substance is then intimately ground with 3 g. of

¹ *Polyt. Zentr.*, 1863, p. 1448.

a mixture of molecular proportions of sodium and potassium carbonate, and the whole transferred to a crucible; 1 g. of potassium or sodium hydroxide is then spread over the surface of the mixture and the latter slowly heated to redness. The mass fuses and becomes inflated, forming a crust on the top, which must, from time to time, be pushed down with a strong platinum wire. After fusion for half an hour the mass is allowed to cool, moistened with water, the thin paste heated nearly to boiling for a quarter of an hour, and filtered; the residue is washed well and the filtrate and washings placed on one side. The residue on the filter paper is dried, transferred to a small flask together with the ash of the filter paper, and about 3 g. of hydrochloric acid of sp. gr. 1.18 added. After a few minutes the contents of the flask will be seen to gelatinise slightly, this being due to the decomposition of alkali silicate, a trace of which is still present. On adding a little more hydrochloric acid, the jelly disappears and the silica then remains in solution. After about an hour's digestion, the contents of the flask are diluted with water and filtered. The residue is washed and now consists of pure carbon which, after being dried and gently ignited, is weighed. The acid filtrate is added to the alkaline filtrate obtained as above, the whole strongly acidified with hydrochloric acid, the liquid evaporated to dryness, and the silica, alumina, and ferric oxide determined in the usual way.¹

APPENDIX.

I. BRONZE PIGMENTS.²

This name is applied to certain powdery substances possessing a metallic lustre and consisting of metallic alloys or compositions such as "Mosaic gold" (stannic sulphide). They are used for coating metallic or other objects, for the purpose of imparting to them a semi-dull metallic lustre. The manufacture of bronze pigments is carried out especially at Fürth and Nuremberg; they are employed in the graphic industries, in the wallpaper and paper industry, and for various other purposes.

The process of manufacture consists in pounding the metal, beaten out into foil, into a fine state of division in special machines. It is then sorted in other machines, according to fineness, and finally polished. The polished powder is then made into a paste with gum solution, passed between granite rollers, and allowed to stand. It settles out of the gum in layers according to the size of grain. After removal of the water the layers are skimmed off, washed with water, dried in a

¹ Cf. also, Donath, *Der Graphit*, 1904.

² Cf. C. Hebing, *Vergoldung und Bronzierung*; G. Buchner, *Die Metallfärbung*, p. 194; L. E. Andrés, *Blattmetalle, Bronzen und Metallpulver*.

specially constructed apparatus, and then coloured by tempering. The coarser powders are known as "brocades." The raw materials used are copper, zinc, and tin, from alloys of which the bronzes are manufactured. For white bronzes aluminium is used. The bronzes exhibit not only the colour of the alloys concerned, but also different shades of orange, red, violet, and green. These shades are temper colours, and are produced almost entirely by heating the bronzes in oil, wax, paraffin, tallow, etc. According to Hebing, the following shades are obtained by the preparation of simple alloys:—Rich gold, pale gold, rich pale gold, green gold, rich green gold, red gold, and copper. By tempering, the following shades are obtained:—Intense yellow, orange, lemon, flame colour, carmine, crimson, brown, rose, lilac, violet, blue, blue-green, and green. For the so-called black bronzes antimony is employed.

Bavarian bronze pigments have been shown to contain the following amounts of copper:—Copper red, 98.92 per cent.; purple, 98.82 per cent.; orange, 95.30 per cent.; pale bronze-yellow, 82.34 per cent.; and intense yellow, 81.55 per cent. The analysis is carried out in the same way as that of a copper alloy containing zinc.

Besides the genuine bronzes, substitutes are also used the oldest of which is "Mosaic gold" (stannic sulphide). They are employed more especially in cases where genuine bronzes, would be injured by acid fumes and hydrogen sulphide.

Tungsten Bronze (Sodium para-tungstate) has been suggested as a substitute for bronze pigments; it possesses a magnificent golden yellow colour; the corresponding potassium salt is purple and in sunlight has a copper-like lustre; the lithium salt has the colour of blue-tempered steel. These substitutes have not, however, as good covering power as the bronze pigments, for, unlike the latter, they do not possess the characteristic cleavage into lamellæ necessary for intense reflection of the coloured rays of light.¹

II. LAKES FROM ARTIFICIAL DYES.²

Lakes are pigment colours which are produced by converting soluble dyes into insoluble compounds. They differ, as regards preparation and composition, from naturally occurring products, such as ochre, umber, etc., and from those which are obtained by the chemical decomposition of salts—*e.g.*, lead chromate, Prussian blue, etc.

Lake Precipitants for Acid Dyes.—The substances most largely employed are:—Barium chloride, lead nitrate or acetate, zinc sulphate, aluminium sulphate or acetate, alum, stannic chloride, antimony pentachloride, calcium nitrate or acetate.

¹ Cf. A. W. Hofmann, *Reports of the Juries of the International Exhibition*, London, 1863, p. 83.

² Cf. *The Manufacture of Lake Pigments from Artificial Colours*, by F. H. Jennison, 1900.

Lake Precipitants for Basic Dyes.—These comprise :—Tannic, phosphoric, arsenious, antimonious, stannic, colophonic, palmitic, and stearic acids.

Lake Bases (Substrata).—These are chiefly :—Barium sulphate, clay, China clay, calcium sulphate, kieselguhr, red lead, zinc oxide, lead sulphate, aluminium hydroxide, calcium carbonate, aluminium phosphate, aluminium arsenite, barium phosphate, lead carbonate, calcium phosphate, lamp black, and viridian.

Examination of the Dyes.—A small quantity of the colour is mixed with glue water or gum, spread on paper, and dried at 40°-50°; the specimen is then compared with standard colours. The surface, which is tested by the feel, and the depth and richness of colour are also examined; these properties, together with the results of examination of the base, often afford hints as to the method of preparation of the lake.

Part of the coloured paper is heated at 100°, in order to observe if the shade changes or if the colour is otherwise affected at this temperature.

Separate pieces of the paper are treated with a drop of 10 per cent. and with stronger nitric and hydrochloric acid and with concentrated and dilute sodium or potassium hydroxide, and the results are referred to Tables of dye tests in order to identify the dye.¹

Ordinary *Yellow lakes* are prepared from naphthol yellow S, auramine, thioflavine T, quinoline yellow, and metanil yellow. Comparative tests with standard samples usually serve as a rapid means for recognition of the dye. The acid test is also of assistance in the identification.

Naphthol Yellow S.—On treatment with hydrochloric acid the colour disappears almost completely. With nitric acid it first becomes reddish, but decolorisation soon follows.

Metanil Yellow.—Hydrochloric acid turns the colour much redder; with nitric acid it turns nearly scarlet.

Auramine.—Both nitric and hydrochloric acid cause almost complete decolorisation.

Quinoline Yellow.—Hydrochloric acid produces scarcely any change; with nitric acid it becomes redder.

Thioflavine T.—Nitric and hydrochloric acids cause decolorisation. With sodium hydroxide it turns redder (auramine is decolorised).

The *Orange Lakes*, almost without exception, are prepared from azo-dyes, such as Mandarin R, G; Orange II; Brilliant orange R, G; Ponceau 4 G. B. L. Very often mixtures are used of a cheap dye to give richness and depth, and a more expensive one to give increased brilliancy and stability. The behaviour towards reagents is practically the same; the examination rests essentially on comparison with

¹ Cf. the section on "Organic Dyes," Vol. II., pp. 1050-1116.

standards. The comparative effect of light during a period of two to three days is a useful test in this case.

Greater difficulties occur in the examination of *Red*, *Scarlet*, and *Crimson Lakes*. The following may be employed for their preparation:—Eosins, alizarin, and azo-dyes, and basic dyes such as safranine, fuchsine, rhodamine, methyl violet, etc.

Eosin Lakes are, after short experience, easily recognised by their vividness, depth of colour, and want of permanence to light. Even after two or three hours' exposure incipient fading may be observed. Treated with acid they become yellow; with alkali the dye is separated from the base; addition of alcohol usually produces a fluorescent solution.

Alizarin Lakes are also coloured yellow by acids, but more slowly. Alkalis cause no change.

Pure *Fuchsine*, *Rhodamine*, and *Safranine Lakes* are easily identified by their characteristic shades; greater difficulties in identification arise when mixtures of dyes are present.

Violet Lakes are prepared from Gallein (these become brown with acids), and more especially from methyl violet. For purposes of shading, rhodamine, fuchsine, etc., are employed.

Blue Lakes are obtained from the various blues—*e.g.*, Nile blue, Methylene blue, Bâle blue, and New blue; also from Water blue, Alkali blue, etc. These dyes are recognised by the reactions given in the Tables in the section on "Organic Dyes," Vol. II., pp. 1050-1116.

Brown Lakes are mostly prepared from Bismark brown toned down with other dyes.

Black Lakes possessing a rich, deep shade are difficult to prepare, and are little used.

Examination of the Substratum.—Admixtures of finely ground mineral substances may generally be detected by feel when the sample is rubbed on paper. For a general analysis a small portion of the dry lake is heated in a porcelain crucible. Arsenic trioxide can be recognised by the garlic-like odour of its vapours. If the residue, after ignition, dissolves almost completely in dilute hydrochloric acid, and, on addition of ammonia to the solution, a precipitate of aluminium hydroxide is formed, it is fairly certain that a lake precipitated on to aluminium arsenite is being dealt with. The presence of a phosphate may be proved by treatment with ammonium molybdate.

For a complete examination, the residue after ignition, the greater part of which is usually soluble in boiling hydrochloric acid, is submitted to qualitative analysis.

An insoluble residue usually consists of clay, barium sulphate, calcium sulphate, or mixtures of these substances.

A full description of the preparation and analysis of Lake Pigments is given by Zerr and Rübencamp.¹

Investigations on the permanence to light of pastel colours will be found in *Veröffentlichungen der technischen Versuchsanstalt für Malerei zu München*.²

¹ *Colour Manufacture*, pp. 429-542.

² *Sitzungsber. K. Akad. München* [5], 16, No. 9.

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APPENDIX

THIS APPENDIX COMPRISES THE TABLES INCLUDED
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TABLE II. (*Text*, p. 128.)

Yield of Hexabromides from Glycerides.

Oil.	Yield of bromides insoluble in ether.	Observer.
	Per cent.	
Linseed oil (iodine value 181)	23·14 ; 23·52	Walker and Warburton
" (" 186·4)	24·17	Lewkowitsch
" (" 190·4)	37·72	"
" 	23·86 to 25·8	Hehner and Mitchell
Tung oil	0	"
" (sample 1)	0	Walker and Warburton
" (" 2)	0·38 ; 0·39	"
Candle nut oil	8·21 ; 7·28	"
Walnut oil	1·42 ; 1·9	Hehner and Mitchell
Poppy seed oil	0	"
Soya bean oil	3·73	Lewkowitsch
Maize oil	0	Hehner and Mitchell
Cotton seed oil	0	"
" 	0	Lewkowitsch
Brazil nut oil	0	Hehner and Mitchell
Almond oil	0	"
Olive oil	0	"
Japan fish oil	21·14 ; 22·07	Walker and Warburton
Fish oil deodorised	49·01 ; 52·28	"
Cod liver oil	42·9	Hehner and Mitchell
" 	35·33 ; 33·76	Walker and Warburton
" (Newfoundland)	32·68 ; 30·62	"
Shark liver oil	22	Hehner and Mitchell
" 	21·22 ; 19·08	Walker and Warburton
Seal oil	27·54 ; 27·92	"
Whale oil	25	Hehner and Mitchell
" (old)	15·54 ; 16·14	Walker and Warburton
" (fresh)	20·1 ; 22·6	Lewkowitsch
Sperm oil	2·61 ; 2·42	Walker and Warburton
" 	3·72 ; 3·69	"
" 	after standing for 48 hours	

TABLE III. (*Text*, p. 132.)

Neutralisation Values of Fatty Acids.

Acid.	Formula.	Molecular weight.	Neutralisation value.
Acetic . . .	$C_2H_4O_2$	60.03	934.5
Butyric . . .	$C_4H_8O_2$	88.06	637.07
Caproic . . .	$C_6H_{12}O_2$	116.10	483.22
Caprylic . . .	$C_8H_{16}O_2$	144.13	389.23
Capric . . .	$C_{10}H_{20}O_2$	172.16	325.85
Lauric . . .	$C_{12}H_{24}O_2$	200.19	280.30
Myristic . . .	$C_{14}H_{28}O_2$	228.22	245.81
Palmitic . . .	$C_{16}H_{32}O_2$	256.26	218.90
Stearic . . .	$C_{18}H_{36}O_2$	284.29	197.33
Oleic . . .	$C_{18}H_{34}O_2$	282.27	198.74
Linolic . . .	$C_{18}H_{32}O_2$	278.24	200.17
Linolenic . . .	$C_{18}H_{30}O_2$	280.26	201.62
Clupanodonic . . .	$C_{18}H_{28}O_2$	276.22	203.09
Ricinoleic . . .	$C_{18}H_{34}O_3$	298.29	188.08
Arachidic . . .	$C_{20}H_{40}O_2$	312.32	179.62
Erucic . . .	$C_{22}H_{42}O_2$	338.34	165.81
Cerotic . . .	$C_{26}H_{52}O_2$	396.42	141.52
Melissic . . .	$C_{30}H_{60}O_2$	452.48	123.98
Hydroxystearic . . .	$C_{18}H_{36}O_3$	300.29	186.81
Dihydroxystearic . . .	$C_{18}H_{36}O_4$	316.29	177.33
Trihydroxystearic . . .	$C_{18}H_{36}O_5$	332.29	168.82
Sativic . . .	$C_{18}H_{36}O_6$	348.29	161.07
Linusic . . .	$C_{18}H_{36}O_8$	380.29	147.51

TABLE IV. (*Text*, p. 135.)

The Iodine Value of Unsaturated Fatty Acids and their Glycerides.

Acid.	Formula.	Iodine value of fatty acid.	Iodine value of		
			Mono- glyceride.	Di- glyceride.	Tri- glyceride.
Tiglic.	$C_5H_8O_2$	253·68	145·79	198·18	225·10
"	$C_{12}H_{22}O_2$	128·88	93·26	112·22	120·39
"	$C_{14}H_{26}O_2$	112·21	85·54	99·84	106·26
Hypogæic	$C_{16}H_{30}O_2$	99·84	77·32	89·93	95·10
Physetoleic					
Lycopodic					
Oleic					
Elaidic	$C_{18}H_{34}O_2$	89·92	71·24	81·80	86·06
Rapic.					
Doeglic	$C_{19}H_{38}O_2$	85·67	68·54	78·28	82·15
Jecoleic					
Erucic	$C_{22}H_{42}O_2$	75·02	61·55	69·28	72·31
Brassicidic					
Linolic	$C_{18}H_{32}O_2$	181·14	143·28	164·68	173·31
Tariric					
Telfairic					
Elæomargaric					
Linolenic	$C_{18}H_{30}O_2$	273·69	216·16	248·65	261·76
Isolinolenic					
Jecoric					
Clupanodonic					
Isanic	$C_{14}H_{20}O_2$	461·19	345·11	409·12	436·08
Ricinoleic	$C_{18}H_{34}O_3$	85·13	68·17	77·79	81·37
Isoricinoleic					
Ricinelaïdic					
Ricinic					
<i>Mixed Triglycerides:—</i>					
Myristopalmito-olein	31·54
Oleodipalmitin	30·43
Oleodimargarin	29·48
Oleopalmitostearin	29·48
Oleodistearin	28·55
Elaidodistearin	28·55
Dioleostearin	57·24

TABLE V. (*Text*, p. 143.)
Some Unsaponifiable Substances and their Characteristics.

	Formula.	Melting point. °C.	Iodine absorption.	Acetates.		Increase of weight on boiling with acetic anhydride.*
				Saponification value.	Melting point. °C.	
Paraffin wax, ceresin	...	38 to 82	3.9 to 4.0†	Per cent. 0
Cetyl alcohol	$C_{16}H_{34}O$	50	0	197.5	22 to 23	17.2
Octadecyl alcohol	$C_{18}H_{38}O$	59	0	180.0	31	15.5
Ceryl alcohol	$C_{26}H_{54}O$	79	0	132.3	65	11.0
Melissyl (myricyl) alcohol.	$C_{30}H_{62}O$	85	0	116.7	70	9.6
Cholesterol	$C_{27}H_{46}O$	148.5	65.8‡	131.1	114	10.9
Isocholesterol	$C_{27}H_{46}O$	137 to 138	(65.8)	131.1	under 100	10.9
Phytosterol, sitosterol	$C_{27}H_{46}O$	137, 138	(65.8)	131.1	125.6 to 137	10.9
Stigmasterol	$C_{30}H_{48}O$	170	119.8**	120.4	141	9.9
Alcohols from sperm oil	?	25.5 to 27.5	64.6 to 65.8§	161 to 190
" carnauba wax	?	88, 90	...	104.9	...	10.2
" wool wax	?	44.4, 48.9	36	136.2	...	10.84
" crude wool wax	?	150.6¶
" beeswax	?	75 to 76; 65 to 66.1	...	99 to 103; 94 to 102	...	6.5 to 7.7; 3.8 to 4.1
Hydrocarbons from beeswax	?	49.5 to 59.2	20 to 22
Alcohols from spermaceti	?	46.7	...	184.9	...	15.64
" insect wax	?	78	...	123.5	...	8.12 to 8.87

* Lewkowitsch, *J. Soc. Chem. Ind.*, 1896, **15**, 14.

† Determined in the author's laboratory.

‡ The author found 67 to 68, using Hübl's solution of iodine. Wijs's solution gave unreliable results, ranging up to more than 145.

§ The iodine values of the fractions into which the mixture of alcohols was separated were found to be as follows: (1) 46.48; (2) 63.3; (3) 69.3; (4) 81.8; (5) 84.9 (*J. Soc. Chem. Ind.*, 1892, **11**, 135).

¶ Iodine value, 44.03.

** Calculated by the author on the assumption that 4 atoms of iodine are taken up, since stigmasterol gives a well-defined tetrabromide.

TABLE VI.

Data for the Identification of

OILS.	Characteristics.							
	Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	Insoluble fatty acids + unsaponifiable matter.
	°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.	Per cent.
Vegetable								
DRYING.								
Linseed	15	0.9315-0.9345	-27	-20	192-195	171-201	...	95.5
Tung oil, Chinese } (Japanese) wood* }	15	0.9360-0.9432	below -17	...	193	150-165	...	92.2
Candle nut . . .	15.5	0.9256	...	liq. at -18	192.6	163.7	...	95.5
Hemp seed . . .	15	0.9255-0.9280	-27	...	192.5	148
Walnut	15	0.9250-0.9260	-27.5	...	195	145	...	95.4
Safflower . . .	15.5	0.9251-0.9280	186.6-193.3	129.8-149.9	1.54 (R.-M.)	95.37
Poppy seed . . .	15	0.9240-0.9270	-18	...	195	133-143	0	95.2
Sunflower . . .	15	0.9240-0.9258	-18.5	...	193.5	119-135	...	95
SEMI-DRYING.								
<i>Cotton seed group—</i>								
Soja bean . . .	15	0.9242-0.9270	-8	...	192.7	137-140	...	95.5
Cameline (German } Sesamé) . . . }	15	0.9200-0.9260	-18	...	188	135-142
Pumpkin seed . .	15	0.9237	-15.5	...	188.4	123-130	...	96.2
Maize	15.5	0.9213-0.9255	-10 to -20	...	188-193	113-125	4.5 (R.-M.)	93-96
Kapok	18	0.9199	181	116	...	94.9
Cotton seed . . .	15	0.9220-0.9250	...	3-4	193-195	103-110	...	95-96
Sesamé	15	0.9230-0.9237	-5	...	189-193	103-108	1.2 (R.-M.)	95.7
Beech nut . . .	15	0.9200-0.9225	-17	...	191-196	104-111	...	95.2
Brazil nut . . .	15	0.9180-0.9185	0.4	...	193.4	106.2
Curcas	15.5	0.9204	-8	...	193.2	98-110	0.5 (R.-M.)	95.3
Croton	15	0.9500	-16	...	210-215	102-104	12-13.6 (R.-M.)	89.0
<i>Rape group—</i>								
Ravison	15.5	0.9183-0.9217	-8	...	174-179	101-122
Hedge mustard .	15	0.9175	-8	...	174	105
Rape (Colza) . .	15.5	0.9132-0.9168	-2 to -10	...	170-179	94-102	0.3	95.1
Black mustard seed	15	0.916-0.920	-17	...	174	96-110	...	95.1
White mustard seed	15.5	0.914-0.916	-8 to -16	...	170-174	92-97	...	96.2
Radish seed . . .	15	0.9175	-10 to -17.5	...	173-178	93-96	0.33 (R.-M.)	95.9
Jamba	15	0.9154	-10 to -12	...	172.3	95.4
NON-DRYING.								
<i>Almond group—</i>								
Cherry kernel . .	15	0.9234	-19 to -20	...	193-195	110-114
Apricot kernel . .	15.5	0.9195	-14	...	192.5	96-108	0	95.4
Plum kernel . . .	15	0.9160-0.9195	-5 to -6	...	191.5	93.3-100.3
Peach kernel . . .	15	0.918-0.9215	below -20	...	192.5	93-109
Almond	15	0.9175-0.9195	-10 to -20	...	191	93-97	...	96.2

* To be separated on the basis of the specific gravities. Cf. Lewkowitsch,

(Text, pp. 146-49.)

Vegetable Oils and of Animal Oils.

		Variables.				Characteristics of fatty acids.									
Refractive index.		Acetyl value.	Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
Butyro-refractometer.															
°C.	Scale divisions.			KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C	
Oils.															
20	84-90	...	3.98	0.8-8.4	0.42-1.1	15.5	0.9233	13-17	19.4 to 20.6	17-21	197	179-182	190-201	60	1.4546
40	72.5	7.6-12	0.44	31; 34	37.2	31 ; 43.8	188.8	144-159
...	20-21
15	76	...	9.86	8.1	0.76	13
...	1.08	15	16.6	18-19	...	141
40	64.8	16	...	16-18	...	150	167
40	65.2	...	16.1	0.33-20
40	63.4	0.7-11	0.43	100	0.8886	16.5	16.2	20.5	199	139	150	60	1.4506
25	72.2	11.2	0.31	18	...	22-24	201.6	124-134	154.3	60	1.4531
...	4.5	0.22	24	...	28	...	119
...	14-13	...	18-20	...	136.8	165.4
25	70.2-72.5	24.5	...	28-29	197
...	7.5 to 8.75	1.7-20.6	1.35-2.86	16-14	...	18-20	198.4	119.5	140-144
...	0.9162	24-23	...	29	191	108
25	67.6-69.4	...	7.6 to 18	0	0.73-1.64	15.5	0.9206 to 0.9219	32-35	32-35	35-38	202-208	111-115	147-151	60	1.4460
25	68	0.23 to 66 (!)	0.95-1.32	23.5	22.9 to 23.8	26-32	200.4	110.45	129-136	60	1.4461
...	17	...	23-24	...	114
25	65	32-25	...	29	...	108
40	56.5	...	7.5	0.7-8.5	0.5-0.58	26.5 to 25.7	28	27.5 to 30.5	...	105.1
27	77.5	...	19-32	...	0.55	16.7	19	...	201	111.5
20	73-74	4.8-12	1.45-1.66	100	0.8802	124.2
25	70.5-71.5
25	68	...	14.7	1.4-13.2	0.58-1	100	0.8758	16	12-13	16-19	185	99-103	121-125	60	1.4991
40	59.5	1.36 to 7.35	15.5	...	16	...	109.6
40	58.5	5.4	15-16	...	95.3
40	57.5	14.5	15-13	...	20	..	97.1
...	16-11	...	19-21	173.9	96.1
...
25	66.6	0.64	15-13	...	19-21	189	109	124.7
...	0.55	0	...	3.4	194	103	111.5
...	15-13	...	20-22	200.5	103 (!)	98.6
25	66.1-67.2	13 to 13.5	10-18	200.9	94-101	101.9
25	64.4	1.5	5	10.1 to 11.8	13-14	204	93-96.5	101.7	60	1.4461
Chemical Technology and Analysis of Oils, Fats and Waxes, 3rd Edition															

TABLE

OILS.	Characteristics.							
	Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	Insoluble fatty acids + unsaponifiable matter.
	°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.	Per cent.
Vegetable								
NON-DRYING (<i>cont.</i>).								
<i>Olive group</i> —Arachis (earth nut) . . .	15	0.9170-0.9209	-3 to 0	0	190-196	83-100	...	95.8
Hazel nut . . .	15	0.9146-0.9170	-17	...	192	83-90	0.99 (R.-M.)	95.6
Olive . . .	15	0.916-0.918	-6 to 2	...	185-196	79-88	0.3	95
Olive kernel . . .	15	0.9184-0.9191	183	87.4
Ben . . .	15	0.9120-0.9198	0	82
<i>Castor group</i> —								
Grape seed . . .	15	0.935	-10 to -13	...	178.5	96	0.46 (R.-M.)	92-13
Castor . . .	15.5	0.9600-0.9679	-10 to -18	...	183-186	83-86	1.4	...
Animal								
MARINE ANIMALS.								
<i>Fish</i> —Menhaden . . .	15.5	0.927-0.933	-4	...	190.6	139-173	1.2	...
Sardine . . .	15	0.9330	161-193	...	94.5
Japanese sardine (Japanese fish oil) . . .	15	0.9160	...	20 to 22	189.8-192.1	100-164	...	96-97
Herring . . .	15.5	0.9202-0.939	171-194	123.5-142	...	95.64
Stickleback	162.0	...	95.78
Sturgeon . . .	15	0.9236	186.3	125.3
Sprat . . .	15.5	0.9284
<i>Liver</i> —Cod . . .	15	0.9210-0.9270	0 to -10	...	171.0-189	167	...	95.3
Haddock . . .	15	0.9298	188.8	154.2	...	93.3
Skate . . .	15	0.9307	185.4	157.3	...	94.7
Tunny	155.9	...	95.79
Shark (Arctic) . . .	15	0.9163	161.0	114.6	...	86.9
Coal fish . . .	15	0.925	177-181	137-162
Hake . . .	15.5	0.9270
Ray . . .	15.5	0.9280
Ling . . .	15	0.9200	184.1	132.6
<i>Blubber</i> —Seal . . .	15	0.9155-0.9263	-2 to -3	...	189-196	127-141	0.07-0.22	95.45
Whale . . .	15.5	0.9250	below -2	...	188.0	121-136	0.7-2.04	93.5
Dolphin (body) . . .	15	0.9180	below -3	...	197.3	99.5	5.6	93.07
Dolphin (jaw)	290	32.8	65.92	66.28
Porpoise (body) . . .	15	0.9258	-16	...	195	...	23.5	...
Porpoise (jaw) . . .	15	0.9258	254-272	22-50	47.77-65.8	70.23
LAND ANIMALS.								
Sheep's foot . . .	15	0.9175	0 to -15	...	194.7	74.2
Horse's foot . . .	15	0.913-0.927	195.9	73.8-90
Neat's foot . . .	15	0.914-0.916	0 to -15	...	194.3	69.3-70.4
Egg . . .	15	0.9144	8 to -10	22.25	184.4-190.2	68.5-81.6	0.4-0.7 (R.-M.)	95.16

VI.—continued.

		Variables.			Characteristics of fatty acids.										
Refractive index.		Acetyl value.	Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
Butyro-refractometer.															
°C.	Scale divisions.			KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C.	

Oils—continued.

25	66-67.5	1.2 to 32 (!)	0.54-0.94	100	0.8790	26	29.2	27.7 to 32	201.6	96-103	105-128	60	1.4461
...	3.2	...	0.5	19-20	...	22-24	200.6	90.3	91.3 to 97.6
25	62.4	...	10.64	1.9-5.0	0.46-1	100	0.8749	22-17	17.2 to 26.4	24-27	193	86-90	95.5 to 103.5	60	1.4410
...	2-3.5
...
...	16.2	20-18	...	24	187.4	99
25	78	146.7 to 150	...	0.14 to 14.61	...	15.5	0.9509	3	...	13	192.1	87-93	106.9	60	1.4546

Oils.

...	11.6	1.6-2.2
...	4-21	0.52-0.86
...	13.0	10-35	0.48-2.6	28.2
...	1.8-4.4	0.99-10.7	178.5
...	21	1.73	181.5
...
25	75	...	4-8	1-25	0.54-7.83	18.4 to 24.3	21-25	204-207	130.5 to 170	...	60	1.4521
...	1.1
...	10.6	...	0.97
...	0.2-3.4	1.0-1.8	177.0
...	11.9	...	10.2
...	1.26 to 1.68
...
...
...	11.0	2.23
...	16.5	1.9-4.0	0.38-1.4	15.5 to 15.9	22-23	193.2
25	70	0.5-3.7	0.92-3.72	100	0.8922	...	23.9	27.0	...	131.2	144.7
...
...
...	3.7
...	5.0	16.4
...	21.1
...	2.86
...	13.0	26.1 to 26.5	29.8 to 30.8	...	61.98 to 63.26
25	68.5	1.2	1.7	34-39	194.9	72.9

TABLE VII.

Data for the Identification of

FATS.*	Characteristics.							
	Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	Insoluble fatty acids + unsaponifiable matter.
	°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.	Per cent.
VEGETABLE.								
<i>Laurel oil group—</i>								
Laurel oil	15	0.9332	25	32-34	197.9	68-80	1.6	...
Mahua butter	100	0.8981	19-22	28-31	190-194	53-67	0.5-0.9	94.82
	(100=1)						(R.-M.)	
Mowrah seed oil	15	0.9175	36	42	188-192	50-62	...	94.76
Macassar oil	15	0.9240	10	22	221.5	48-55	...	91.5
Shea butter (Galam butter)	15	0.9175	17-18	25.3	179-192	56.6	...	94.76
Palm oil	15	0.921-0.9245	...	27-42.5	196-202	51.5	0.5	94.97
Nutmeg butter	15	0.945-0.996	41-42	38-51	154-191	40-52 (50-81)	1.4.2 (R.-M.)	...
<i>Cocoa group—Mkányi.</i>	15	0.9298	38	40-41	190.5	41.9	1.21 (R.-M.)	95.65
Malabar tallow	15	0.9150	30.5	36.5	188.7-192	38.2	...	0.2 to 0.44 (R.-M.)
Cocoa butter	15	0.9500-0.976	23-21.5	28-33	193.55	32-41	0.2-0.8 (R.-M.)	94.59
Chinese vegetable tallow	15	0.9180	27-31	36-46	200.3	28-37
Kokum butter (Goa butter)	40	0.8952	37.6 to 37.9	41-42	187-191	33.6	0.1-1.5 (R.-M.)	95.1
	(15=1)							
Borneo tallow	35-42	...	(31?)
<i>Cocoa nut oil group—</i>								
Mocaya oil	22	24-29	240.6	24.63	7.0 (R.-M.)	...
Maripa	100	0.8686	24-25	26.5 to 27.0	270.5	17.35	4.45 (R.-M.)	88.88
	(15.5=1)							
Palm seed oil	15	0.9520	20.5	23-28	242-250	13-14	5.6 (R.-M.)	87.6 to 91.1
	(15.5=1)							
Cocoa nut oil	40	0.9115	22-14	21-24	246-260	8-9.5	7.8.4 (R.-M.)	88.6-90
	(15.5=1)							
Myrtle wax	15	0.995	39-43	40-44	208.7	10.7
Japan wax	15	0.9700-0.980	48.5-53	50-54	217-237.5	4.9-8.5	...	90.6
Dika oil (oba oil, wild mango oil)	0.8200	34.8	41.6	...	31.1
ANIMAL.								
<i>Drying—Polar bear</i>	15	0.9256	187.9	147
<i>Semi-drying—</i>								
Black cock	15	0.9296	201.6	121.1	2.1	...
Hare	15	0.9349	17-23	35-40	200.9	102.2	1.59	95.4
Rabbit (wild)	15	0.9393	17-22	35-38	199.3	99.8	0.7	...
" (tame)	15	0.9342	22-24	40-42	202.6	67.6	2.8	95.5
Wild duck	15-20	...	198.5	84.6	1.3	...
Tame duck	22-24	36-39	...	58.5
Horse	15	0.9189	43-30	34-54	195-197	71-86	0.2-0.4	95-96

* For subsidiary groups, cf. J. Lewkowitsch, *Bull. Soc. Chim.*, 1909, 42. (Conference: Fatty Compounds.)

(Text, pp. 150-53.)

Vegetable and Animal Fats.

		Variables.			Characteristics of fatty acids.									
Refractive index.		Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
Butyro-refractometer.														
°C.	Scale divisions.	KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C.		
...	26.3	15.1	81.8	
40	52.1	
...	34.56	38.40	40.3	45	...	56.6	
...	6.2 to 35.4	3.12	51.6 to 53.2	52-55	191.6	50-58	103.2	...	
...	29.4	3.5	38	53.8	58	...	56-57.2	
...	...	18	24-200	...	100	0.8701	...	35.9 to 45.5	47-50	205.6	53.3	94.6	...	
40	48-85	...	17-44.8	40	35.9	42.5	
...	23.3	57.5	61.5	59 to 61.5	...	42.1	
...	38	54.8	...	56.6	
40	46-47.8	2.8	1.1 to 1.88	47-45	48.3	48-50	190	33-39	...	60 1.422	
...	2.2-7.5	45.2 to 53.5	53-57	182-208	30-39	
25	1.4628	...	21	59.4	...	60-61	198.9	
...	20	53.5 to 54	
...	22-20	...	23-25	254	
...	100	0.8230	25	...	27.5 to 28.5	...	12.15	
40	36.5	1.9 to 8.4	8.36	...	(15.5=1)	20.5 to 25.5	25 to 28.5	258-264	12.0	...	60 1.4310	
40	+34	0.9 to 12.3	5-50	...	98-99 (15.5=1)	0.8354	20-16	22.5 to 25.2	25-27	258-266	8.4-9.3	18.6	60 1.4295	
...	3-4.4	46	...	47.5	230.9	
...	...	27 to 31.2	7.33	1.1 to 1.63	98-99 (15.5=1)	0.8480	53.0 to 56.5	59.4	56-62	213.7	
...	19.6	
...	
...	5.9	...	15	0.9374	25-28	...	30-33	199.3	120	
40	49	...	2.73	...	15	0.9361	36-40	...	44-47	209	93.3	...	But'r. refr. 36	
...	7.2	...	15	0.9246	35-36	...	39-41	209.5	101.1	
40	49	...	6.2	...	15	0.9264	37-39	...	40-42	218.1	64.4	...	But'r. refr. 36	
...	1.5	30-31	...	36-40	
...	
40	53.7	...	0-2.44	37.7	33.7	37.5 to 39.5	202.6	84-87	

TABLE

FATS.	Characteristics.							
	Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	Insoluble fatty acids + unsaponifiable matter.
	°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.	Per cent.
ANIMAL (<i>cont.</i>). <i>Non-drying—</i>								
Horse marrow . . .	15	0·9204-0·9221	24-20	35-39	199·8	79·1	1	...
Goose (domestic) . .	15	0·9274	18-20	32-34	193·1	67-71	0·98	95
Wild goose . . .	15	0·9158	18-20	...	196	99·6	0·2-0·3 (R.-M.)	...
Lard	15	0·934-0·938	27·1 to 29·9	36-40·5	195·4	50-70	...	93-96
Wild boar	15	0·9424	22-23	40-44	195·1	76·6	0·68	...
Beef marrow . . .	15	0·9311-0·9380	31-29	37-45	199	55·4	1·1	...
Bone	15	0·914-0·916	15-17	21-22	190·9	46-55·8
Beef tallow . . .	15	0·943-0·952	35-27	45-40	193·2-200	38-46	0·25	95·6
Mutton tallow . .	15	0·937-0·953	36-41	44-45	192-195·2	35-46	...	95·5
Butter	15	0·926-0·940	20-23	28-33	227	26-38	12·5-15·2	86·5 to 89·8
Stag	15	0·9670	39-48	49-52	199·9	20·5-25·7	1·66	...

TABLE VIII.

Data for the

WAXES.	Characteristics.							
	Sp. gr.		Solidifying point.	Melting point.	Saponification value.	Iodine value.	Reichert (R.) or Reichert-Meissl (R.-M.) value.	
	°C.		°C.	°C.	KOH. mg.	Per cent.	N/10 KOH. c.c.	
<i>Liquid—</i>								
Sperm oil	15	0·8799-0·8835	125·2-132·6	81-90	1·3	
Bottlenose oil . .	15	0·8764	123-135·9	67-82·1	1·4	
<i>Vegetable—</i>								
Carnaüba	15	0·990-0·999	80-81	85-86	79-95	13·5	...	
<i>Animal—</i>								
Wool (wool fat) .	17	0·9413-0·9449	30-30·2	31-35	102·4	17·1-28·9	...	
Bees	15	0·964-0·970	60·5-62·8	61·5-64·4	90-98	7·9-11	0·34-0·54	
Spermaceti . . .	15	0·905-0·960	42-47	42-49	123-135	
Insect (Chinese) .	15	0·926-0·970	80·5-81	80·5-83	80·5-93	

VII.—*continued.*

Refractive index.		Variables.			Characteristics of fatty acids.									
		Acetyl value.	Acid value.	Unsaponifiable matter.	Sp. gr.		Solidifying point.		Melting point.	Neutralisation value.	Iodine value.		Refractive index.	
°C.	Scale divisions.		KOH. mg.	Per cent.	°C.		°C.	Titre. °C.	°C.	KOH. mg.	Total fatty acids.	Liquid fatty acids.	°C	
...	1	...	15	0.9182 to 0.9289	36-34	...	42-44	210.8 to 217.6	71.8 to 72.2
40	50-50.5	...	0.59	...	15	0.9257	31-32	...	38-40	202.4	65.3
...	0.86	...	15	0.9251	33-34	...	34-40	196.4	65.1
40	48.6 to 51.2	2.6	0.54 to 1.28	0.23	99	0.8445	39	41-42	43-44	201.8	64	92.1* 90-106†	60	1.4395
...	2.6	...	15	0.9333	32.5 to 33.5	...	39-40	203.6	81.2	
...	...	4.2	1.6	...	15	0.9300 to 0.9399	37.9 to 38	...	44-46	204.5	55.5
...	...	11.3	29.6-53	0.5 to 1.8	28	...	30	200	55.7 to 57.4
40	49	2.7 to 8.6	3.5-50	...	100 (100=1)	0.8698	...	37.9 to 46.2	43-44	197.2	41.3	92.4	60	1.4375
...	1.7-14	41	40.15 to 48.2	49-50	210	34.8	92.7	60	1.4374
40	41-42	1.9 to 8.6	0.45 to 35.38	...	37.75 (15.5=1)	0.9075	33-38	...	38-40	210-220	28-31	...	60	1.437
40	44.5	...	3.5	...	15	0.9685	46-48	...	50-52	201.3	23.6

* European lard.

† American lard.

(*Text*, pp. 152-53.)

Identification of Waxes.

[illegible]

TABLE IX. (*Text*, p. 158.)

Titration Values of Butter Fats. (Polenske.)

Titration values, i.e., number of c.c. N/10 KOH required for the neutralisation of the:—								
No.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.	Soluble volatile acids (Reichert-Meissl value).	Insoluble volatile acids.
	Pure butter fat.		Same butter fat with addition of 10 per cent. cocoa-nut oil.		Same butter fat with addition of 15 per cent. cocoa-nut oil.		Same butter fat with addition of 20 per cent. cocoa-nut oil.	
1	19.9	1.35	18.7	2.4	18.1	2.9	17.6	3.3
2	21.1	1.4	19.7	2.3	19.2	3.0	18.5	3.6
3	22.5	1.5	21.0	2.5	20.4	2.9	19.8	3.5
4	23.3	1.6	22.0	2.5	21.5	3.1	21.0	3.7
5	23.4	1.5	22.3	2.4	21.7	3.1	21.2	3.7
6	23.6	1.7	22.5	2.5	21.9	3.3	21.4	4.0
7	24.5	1.6	23.3	2.5	22.4	3.1	21.7	3.7
8	24.7	1.7	23.8	2.9	22.9	3.5	22.1	3.9
9	24.8	1.7	23.5	2.7	22.7	3.2
10	24.8	1.6	23.4	2.5	22.8	3.0	22.1	3.6
11	25.0	1.8	23.0	2.7	23.3	3.1	21.8	3.6
12	25.1	1.6	23.5	2.5	23.1	3.0	22.5	3.8
13	25.2	1.6	23.4	2.6	22.9	3.0	22.3	3.7
14	25.3	1.8	24.0	2.9	23.5	3.5	22.6	4.1
15	25.4	1.9	24.2	3.0	23.7	3.6	22.6	4.1
16	25.6	1.7	24.1	2.7	23.3	3.1	22.7	3.7
17	25.4	1.7	23.8	2.6	23.0	3.1
18	26.2	1.9	25.0	3.1	24.2	3.6	23.6	4.0
19	26.5	1.9	25.0	2.9	24.1	3.5	23.2	4.1
20	26.6	1.8	25.4	2.9	24.6	3.3	23.9	3.8
21	26.7	2.0	25.2	3.2	24.5	3.6	23.7	4.2
22	26.8	2.0	24.8	3.0	24.2	3.4	23.5	4.0
23	26.9	2.1	25.2	2.9	24.1	3.6	23.2	4.2
24	26.9	1.9	24.9	2.9	24.0	3.3	23.3	4.0
25	27.5	1.9	25.7	2.7	24.9	3.3	24.0	3.9
26	27.8	2.2	26.0	3.1	25.0	3.7
27	28.2	2.3	26.1	3.1	25.1	3.8	24.5	4.4
28	28.4	2.3	26.5	3.5	25.7	4.0	25.1	4.5
29	28.8	2.2	26.8	3.3	26.0	3.9
30	28.8	2.5	27.1	3.5	26.3	4.0	25.4	4.7
31	29.4	2.6	27.6	3.8	26.9	4.2
32	29.6	2.8	27.5	3.8	26.2	4.2	25.5	4.9
33	29.5	2.5	27.4	3.5	26.6	4.1	25.4	4.7
34	30.1	3.0	27.8	3.8	26.9	4.4	26.2	5.0

TABLE X. (*Text, p. 168.*)
Some Characteristics and Variables of Gum Resins. (Lewkowitsch.)

	Original resins.						After heating to 300°.				
	Acid value.	Saponification value.	Unsaponifiable matter.	Iodine value.		Solubility in alcohol.	Acid value.	Saponification value.	Unsaponifiable matter.	Iodine value.	
				By ICl.	By Br.					By ICl.	By Br.
Commercial copal .	109.8	143.1	Per cent. 7.96	135.5	183.6	Per cent. 93.06	26.49	85.4	Per cent. 14.73	124.3	181.3
”	42.43	66.82	14.99	191.2	114.6	54.83	24.94	61.04	46.40	143.7	233.5
Copal (Sierra Leone)	72.83	119.03	18.81	105.7	96.05	...	12.89	114.9	17.22	125.5	173.6
” (Manilla)	127.6	175.17	15.98	137.9	188.2	...	68.21	136.3	22.99	133.3	186.4
” (Brazilian)	108.99	171.4	7.66	127.7	72.66	...	46.25	113.8	38.74	136.7	225.9
” (Sierra Leone)	65.7	110.5	16.27	94.55	117.0	...	15.32	123.8	22.31	95.23	135.4
Kauri .	37.39	53.84	20.07	90.99	17.14	61.07	10.39	67.70	74.71
Mastic .	52.73	81.79	51.13	175.7	185.0	84.41	23.23	50.24	49.28	165.0	217.8
Snellac (dark)	61.13	203.0	3.56	35.57	13.25
Sandarac (Mogador)	134.39	143.42	13.2	112.2	99.98	...	64.84	136.14	14.28	126.4	69.13
” (Australian)	131.15	134.32	17.44	125.4	63.83	...	106.6	137.26	9.93
Animi (No. 1)	18.69	73.15	6.3	105.3	182.7	...	9.25	53.73	...	106.1	207.4
” (No. 2)	30.22	93.5	6.85	96.21	95.85
Dammar	35.22	32.73	75.96	127.5	169.4	...	10.85	60.44	86.57	127.0	196.8
Amber .	16.7	121.27	18.86	53.98	82.82
“Succinite” .	11.24	113.68	7.06	55.05	78.4	...	10.60	99.19	16.25	74.34	147.8
Colophony	146.46	153.01	15.94	133.7	302.1

TABLE XI. (*Text*, p. 181.)

Melting Points of Candle Material from "Mixed Paraffin Wax"
(Scotch Pyroparaffin) and "Stearine." (I. I. Redwood.)

Paraffin wax.		"Stearine."		Mixture.
Per cent.	Melting point.	Per cent.	Melting point.	Melting point.
	° F.		° F.	° F.
90	102	10	121	100·0
80	102	20	121	98·5
70	102	30	121	100·0
60	102	40	121	104·5
50	102	50	121	110·5
40	102	60	121	111·0
30	102	70	121	113·5
20	102	80	121	117·5
10	102	90	121	119·0
90	120	10	123	118·0
80	120	20	123	116·50
70	120	30	123	114·0
60	120	40	123	112·0
50	120	50	123	110·0
40	120	60	123	109·0
30	120	70	123	113·0
20	120	80	123	118·50
10	120	90	123	119·50
90	120·25	10	129·75	118·50
80	120·25	20	129·75	116·75
70	120·25	30	129·75	114·50
60	120·25	40	129·75	112·25
50	120·25	50	129·75	113·0
40	120·25	60	129·75	118·75
30	120·25	70	129·75	122·0
20	120·25	80	129·75	124·50
10	120·25	90	129·75	127·0
90	125	10	121	123·0
80	125	20	121	121·0
70	125	30	121	119·0
60	125	40	121	117·50
50	125	50	121	114·0
40	125	60	121	111·0
30	125	70	121	107·0
20	125	80	121	114·0
10	125	90	121	117·0
90	130	10	121	128·0
80	130	20	121	125·50
70	130	30	121	123·0
60	130	40	121	121·0
50	130	50	121	118·50
40	130	60	121	114·0
30	130	70	121	109·0
20	130	80	121	115·50
10	130	90	121	118·0
90	132·50	10	129·75	130·50
80	132·50	20	129·75	128·50
70	132·50	30	129·75	126·50
60	132·50	40	129·75	124·25
50	132·50	50	129·75	121·0
40	132·50	60	129·75	117·75
30	132·50	70	129·75	119·50
20	132·50	80	129·75	125·25
10	132·50	90	129·75	127·50

TABLE XII. (*Text*, p. 182.)

Melting Points of Candle Material from Saxo-Thuringian "Paraffin Wax" and "Stearine." (W. Scheithauer.)

Paraffin wax.		"Stearine."		Mixture.
Per cent.	Melting point.	Per cent.	Melting point.	Melting point.
	°C.		°C.	°C.
90·0 66·6 33·3 10·0	36·5	10·0 33·3 66·6 90·0	54	36·5 39·0 45·75 51·75
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		36·5 35·5 47·0 52·0
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		39·75 40·5 47·5 52·0
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		44·0 40·75 48·0 52·5
90·0 66·6 33·3 10·0	48·5	10·0 33·3 66·6 90·0	54	47·5 45·0 47·75 52·5
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		49·0 47·0 47·5 52·5
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		53·0 49·0 47·0 52·5
90·0 66·6 33·3 10·0		10·0 33·3 66·6 90·0		55·5 62·0 47·5 52·5

TABLE XIII. (*Text*, p. 205.)

Specific Gravities of Aqueous Solutions of Chemically pure Glycerin.

Glycerol. Per cent.	Lenz.	Strohmer.	Gerlach.		Nicol.
	Sp. gr. at 12° to 14° C. Water at 12° = 1.	Sp. gr. at 17°·5 C. Water at 17°·5 = 1.	Sp. gr. at 15° C. Water at 15° = 1.	Sp. gr. at 20° C. Water at 20° = 1.	Sp. gr. at 20° C. Water at 20° = 1.
100	1·2691	1·262	1·2653	1·2620	1·26348
99	1·2664	1·259	1·2628	1·2594	1·26091
98	1·2637	1·257	1·2602	1·2568	1·25832
97	1·2610	1·254	1·2577	1·2542	1·25572
96	1·2584	1·252	1·2552	1·2516	1·25312
95	1·2557	1·249	1·2526	1·2490	1·25052
94	1·2531	1·246	1·2501	1·2464	1·24790
93	1·2504	1·244	1·2476	1·2438	1·24526
92	1·2478	1·241	1·2451	1·2412	1·24259
91	1·2451	1·239	1·2425	1·2386	1·23990
90	1·2425	1·236	1·2400	1·2360	1·23720
89	1·2398	1·233	1·2373	1·2333	1·23449
88	1·2372	1·231	1·2346	1·2306	1·23178
87	1·2345	1·228	1·2319	1·2279	1·22907
86	1·2318	1·226	1·2292	1·2252	1·22636
85	1·2292	1·223	1·2265	1·2225	1·22365
84	1·2265	1·220	1·2238	1·2198	1·22094
83	1·2238	1·218	1·2211	1·2171	1·21823
82	1·2212	1·215	1·2184	1·2144	1·21552
81	1·2185	1·213	1·2157	1·2117	1·21281
80	1·2159	1·210	1·2130	1·2090	1·21010
79	1·2122	1·207	1·2102	1·2063	1·20739
78	1·2106	1·204	1·2074	1·2036	1·20468
77	1·2079	1·202	1·2046	1·2009	1·20197
76	1·2042	1·199	1·2018	1·1982	1·19925
75	1·2016	1·196	1·1990	1·1955	1·19653
74	1·1999	1·193	1·1962	1·1928	1·19381
73	1·1973	1·190	1·1934	1·1901	1·19109
72	1·1945	1·188	1·1906	1·1874	1·18837
71	1·1918	1·185	1·1878	1·1847	1·18565
70	1·1889	1·182	1·1850	1·1820	1·18293
69	1·1858	1·179	1·18020
68	1·1826	1·176	1·17747
67	1·1795	1·173	1·17474
66	1·1764	1·170	1·17201
65	1·1733	1·167	1·1711	1·1685	1·16928
64	1·1702	1·163	1·16654
63	1·1671	1·160	1·16380
62	1·1640	1·157	1·16107
61	1·1610	1·154	1·15834
60	1·1582	1·151	1·1570	1·1550	1·15561
59	1·1556	1·149	1·15288
58	1·1530	1·146	1·15015
57	1·1505	1·144	1·14742
56	1·1480	1·142	1·14469
55	1·1455	1·140	1·1430	1·1415	1·14196
54	1·1430	1·137	1·13923
53	1·1403	1·135	1·13650
52	1·1375	1·133	1·13377
51	1·1348	1·130	1·13104
50	1·1320	1·128	1·1290	1·1280	1·12831
45	1·1183	...	1·1155	1·1145	1·11469
40	1·1045	...	1·1020	1·1010	1·10118
35	1·0907	...	1·0885	1·0875	1·08786
30	1·0771	...	1·0750	1·0740	1·07469
25	1·0635	...	1·0620	1·0610	1·06166
20	1·0498	...	1·0490	1·0480	1·04884
15	1·0374	1·03622
10	1·0245	...	1·0245	1·0235	1·02391
5	1·0123	1·01184
0	1·0000	...	1·0000	1·0000	1·00000

TABLE XV. (*Text*, p. 207.)

Differences between the Refractive Indices of
Aqueous Solutions of Glycerin and Pure
Water. (Lenz.)

n_D glycerol. - n_D water.	Per cent. of glycerol by weight.	n_D glycerol. - n_D water.	Per cent. of glycerol by weight.	n_D glycerol. - n_D water.	Per cent. of glycerol by weight.	n_D glycerol. - n_D water.	Per cent. of glycerol by weight.
0.1424	100	0.1046	74	0.0645	48	0.0288	22
0.1410	99	0.1032	73	0.0630	47	0.0275	21
0.1395	98	0.1018	72	0.0616	46	0.0261	20
0.1381	97	0.1003	71	0.0601	45	0.0238	19
0.1366	96	0.0987	70	0.0587	44	0.0225	18
0.1352	95	0.0970	69	0.0572	43	0.0212	17
0.1337	94	0.0952	68	0.0556	42	0.0199	16
0.1323	93	0.0933	67	0.0541	41	0.0186	15
0.1308	92	0.0915	66	0.0526	40	0.0173	14
0.1294	91	0.0897	65	0.0510	39	0.0160	13
0.1279	90	0.0889	64	0.0495	38	0.0146	12
0.1264	89	0.0861	63	0.0479	37	0.0133	11
0.1250	88	0.0842	62	0.0464	36	0.0120	10
0.1235	87	0.0824	61	0.0451	35	0.0108	9
0.1221	86	0.0806	60	0.0438	34	0.0096	8
0.1206	85	0.0792	59	0.0424	33	0.0083	7
0.1191	84	0.0780	58	0.0411	32	0.0071	6
0.1177	83	0.0768	57	0.0398	31	0.0058	5
0.1162	82	0.0757	56	0.0358	30	0.0046	4
0.1148	81	0.0745	55	0.0372	29	0.0033	3
0.1133	80	0.0731	54	0.0385	28	0.0021	2
0.1119	79	0.0717	53	0.0345	27	0.0008	1
0.1104	78	0.0702	52	0.0332	26	0.0000	0
0.1090	77	0.0688	51	0.0318	25		
0.1075	76	0.0663	50	0.0315	24		
0.1061	75	0.0659	49	0.0302	23		

TABLE XVI. (*Text*, p. 306.)

Specific Gravities of Acetic Acid at 15°. (Oudemans.)

Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.
1·0007	1	1·0363	26	1·0623	51	1·0747	76
1·0022	2	1·0375	27	1·0631	52	1·0748	77
1·0037	3	1·0388	28	1·0638	53	1·0748	78
1·0052	4	1·0400	29	1·0646	54	1·0748	79
1·0067	5	1·0412	30	1·0653	55	1·0748	80
1·0083	6	1·0424	31	1·0660	56	1·0747	81
1·0098	7	1·0436	32	1·0666	57	1·0746	82
1·0113	8	1·0447	33	1·0673	58	1·0744	83
1·0127	9	1·0459	34	1·0679	59	1·0742	84
1·0142	10	1·0470	35	1·0685	60	1·0739	85
1·0157	11	1·0481	36	1·0691	61	1·0736	86
1·0171	12	1·0492	37	1·0697	62	1·0731	87
1·0185	13	1·0502	38	1·0702	63	1·0726	88
1·0200	14	1·0513	39	1·0707	64	1·0720	89
1·0214	15	1·0523	40	1·0712	65	1·0713	90
1·0228	16	1·0533	41	1·0717	66	1·0705	91
1·0242	17	1·0543	42	1·0721	67	1·0696	92
1·0256	18	1·0552	43	1·0725	68	1·0686	93
1·0270	19	1·0562	44	1·0729	69	1·0674	94
1·0284	20	1·0571	45	1·0733	70	1·0660	95
1·0298	21	1·0580	46	1·0737	71	1·0644	96
1·0311	22	1·0589	47	1·0740	72	1·0625	97
1·0324	23	1·0598	48	1·0742	73	1·0604	98
1·0337	24	1·0607	49	1·0744	74	1·0580	99
1·0350	25	1·0615	50	1·0746	75	1·0553	100

TABLE XVII. (*Text*, p. 557.)

For calculating the Percentage of Invert Sugar in the presence of Sucrose from the weight of Copper obtained, 10 g. of substance being used.

Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
50	0·05	120	0·40	190	0·79	260	1·19
55	0·07	125	0·43	195	0·82	265	1·21
60	0·09	130	0·45	200	0·85	270	1·24
65	0·11	135	0·48	205	0·88	275	1·27
70	0·14	140	0·51	210	0·90	280	1·30
75	0·16	145	0·53	215	0·93	285	1·33
80	0·19	150	0·56	220	0·96	290	1·36
85	0·21	155	0·59	225	0·99	295	1·38
90	0·24	160	0·62	230	1·02	300	1·41
95	0·27	165	0·65	235	1·05	305	1·44
100	0·30	170	0·68	240	1·07	310	1·47
105	0·32	175	0·71	245	1·10	315	1·50
110	0·35	180	0·74	250	1·13		
115	0·38	185	0·76	255	1·16		

TABLE XVIII. (*Text*, p. 558.)

For calculating the Percentage of Invert Sugar in the presence of Sucrose from the weight of Copper obtained, 5 g. of substance being used. (Baumann.)

Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.	Cu.	Invert sugar.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
(35)	(0·04)	110	0·83	185	1·65	260	2·50
40	0·09	115	0·88	190	1·70	265	2·56
45	0·14	120	0·93	195	1·76	270	2·62
50	0·19	125	0·99	200	1·82	275	2·68
55	0·25	130	1·04	205	1·87	280	2·74
60	0·30	135	1·10	210	1·93	285	2·79
65	0·35	140	1·15	215	1·98	290	2·85
70	0·40	145	1·21	220	2·04	295	2·91
75	0·45	150	1·26	225	2·10	300	2·97
80	0·51	155	1·31	230	2·16	305	3·03
85	0·56	160	1·37	235	2·21	310	3·09
90	0·61	165	1·42	240	2·27	315	3·15
95	0·66	170	1·48	245	2·33	320	3·21
100	0·72	175	1·54	250	2·39		
105	0·77	180	1·59	255	2·44		

TABLE XIX. (*Text*, p. 560.)

Table giving the Factors to be used in Calculations for the Determination of Invert Sugar in presence of Sucrose. (E. Hiller.)

Invert sugar in 100 parts of total sugar = B.	Milligrams of invert sugar = A.						
	200	175	150	125	100	75	50
100	56.4	55.4	54.5	53.8	53.2	53.0	53.0
90	56.3	55.3	54.4	53.8	53.2	52.9	52.9
80	56.2	55.2	54.3	53.7	53.2	52.7	52.7
70	56.1	55.1	54.2	53.7	53.2	52.6	52.6
60	55.9	55.0	54.1	53.6	53.1	52.5	52.4
50	55.7	54.9	54.0	53.5	53.1	52.3	52.2
40	55.6	54.7	53.8	53.2	52.8	52.1	51.9
30	55.5	54.5	53.5	52.9	52.5	51.9	51.6
20	55.4	54.3	53.3	52.7	52.2	51.7	51.3
10	54.6	53.6	53.1	52.6	52.1	51.6	51.2
9	54.1	53.6	52.6	52.1	51.6	51.2	50.7
8	53.6	53.1	52.1	51.6	51.2	50.7	50.3
7	53.6	53.1	52.1	51.2	50.7	50.3	49.8
6	53.1	52.6	51.6	50.7	50.3	49.8	48.9
5	52.6	52.1	51.2	50.3	49.4	48.9	48.5
4	52.1	51.2	50.7	49.8	48.9	47.7	46.9
3	50.7	50.3	49.8	48.9	47.7	46.2	45.1
2	49.9	48.9	48.5	47.3	45.8	43.3	40.0
1	47.7	47.3	46.5	45.1	43.3	41.2	38.1

TABLE XX. (*Text*, p. 562.)

For calculating the Percentage of Sucrose, corresponding to the Invert Sugar present, from the amount of Copper obtained, the duration of boiling being three minutes, and the amount of substance used being 0.1625 g. (Herzfeld.)

Copper.	Sucrose.	Copper.	Sucrose.	Copper.	Sucrose.	Copper.	Sucrose.
mg.	Per cent.	mg.	Per cent.	mg.	Per cent.	mg.	Per cent.
79	24.57	126	38.87	173	53.63	220	68.87
80	24.87	127	39.18	174	53.95	221	69.20
81	25.17	128	39.49	175	54.27	222	69.53
82	25.47	129	39.80	176	54.59	223	69.87
83	25.78	130	40.11	177	54.91	224	70.20
84	26.08	131	40.42	178	55.23	225	70.53
85	26.38	132	40.73	179	55.55	226	70.86
86	26.68	133	41.04	180	55.87	227	71.19
87	26.98	134	41.35	181	56.19	228	71.53
88	27.29	135	41.66	182	56.51	229	71.86
89	27.59	136	41.98	183	56.83	230	72.19
90	27.89	137	42.29	184	57.15	231	72.52
91	28.19	138	42.60	185	57.47	232	72.85
92	28.50	139	42.91	186	57.79	233	73.18
93	28.80	140	43.22	187	58.11	234	73.51
94	29.10	141	43.53	188	58.43	235	73.85
95	29.40	142	43.85	189	58.75	236	74.18
96	29.71	143	44.16	190	59.07	237	74.51
97	30.02	144	44.48	191	59.39	238	74.84
98	30.32	145	44.79	192	59.72	239	75.17
99	30.63	146	45.10	193	60.04	240	75.50
100	30.93	147	45.42	194	60.36	241	75.83
101	31.24	148	45.73	195	60.69	242	76.17
102	31.54	149	46.05	196	61.01	243	76.51
103	31.85	150	46.36	197	61.33	244	76.84
104	32.15	151	46.68	198	61.65	245	77.18
105	32.45	152	46.99	199	61.98	246	77.51
106	32.76	153	47.30	200	62.30	247	77.85
107	33.06	154	47.62	201	62.63	248	78.18
108	33.36	155	47.93	202	62.95	249	78.52
109	33.67	156	48.25	203	63.28	250	78.85
110	33.97	157	48.56	204	63.60	251	79.19
111	34.27	158	48.88	205	63.93	252	79.53
112	34.58	159	49.19	206	64.26	253	79.88
113	34.88	160	49.50	207	64.58	254	80.22
114	35.19	161	49.82	208	64.91	255	80.56
115	35.49	162	50.13	209	65.23	256	80.90
116	35.80	163	50.45	210	65.56	257	81.24
117	36.10	164	50.76	211	65.89	258	81.59
118	36.41	165	51.08	212	66.22	259	81.93
119	36.71	166	51.40	213	66.55	260	82.27
120	37.01	167	51.72	214	66.88	261	82.61
121	37.32	168	52.04	215	67.21	262	82.95
122	37.63	169	52.35	216	67.55	263	83.30
123	37.94	170	52.67	217	67.88	264	83.64
124	38.25	171	52.99	218	68.21	265	83.98
125	38.56	172	53.31	219	68.54	266	84.32

TABLE XXI.¹ (*Text*, pp. 571-76.)

For comparison between the Percentage Weight or Degrees according to Brix, Specific Gravity, and Degrees according to Baumé, for pure Sugar Solutions from 0 to 95 per cent.; Temperature: 17°.5. (Scheibler and Matejczek.)

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
0.0	1.00000	0.0	0.0	4.1	1.01610	2.3	2.3	8.2	1.03270	4.6	4.6
0.1	1.00038	0.1	0.1	4.2	1.01650	2.4	2.3	8.3	1.03311	4.7	4.6
0.2	1.00077	0.1	0.1	4.3	1.01690	2.4	2.4	8.4	1.03352	4.8	4.7
0.3	1.00116	0.2	0.2	4.4	1.01730	2.5	2.4	8.5	1.03393	4.8	4.7
0.4	1.00155	0.2	0.2	4.5	1.01770	2.55	2.5	8.6	1.03434	4.9	4.8
0.5	1.00193	0.3	0.3	4.6	1.01810	2.6	2.6	8.7	1.03475	4.9	4.8
0.6	1.00232	0.3	0.3	4.7	1.01850	2.7	2.6	8.8	1.03517	5.0	4.9
0.7	1.00271	0.4	0.4	4.8	1.01890	2.7	2.7	8.9	1.03558	5.0	4.9
0.8	1.00310	0.45	0.4	4.9	1.01930	2.8	2.7	9.0	1.03599	5.1	5.0
0.9	1.00349	0.5	0.5	5.0	1.01970	2.8	2.8	9.1	1.03640	5.2	5.0
1.0	1.00388	0.6	0.55	5.1	1.02010	2.9	2.8	9.2	1.03682	5.2	5.1
1.1	1.00427	0.6	0.6	5.2	1.02051	2.95	2.9	9.3	1.03723	5.3	5.2
1.2	1.00466	0.7	0.7	5.3	1.02091	3.0	2.9	9.4	1.03765	5.3	5.2
1.3	1.00505	0.7	0.7	5.4	1.02131	3.1	3.0	9.5	1.03806	5.4	5.3
1.4	1.00544	0.8	0.8	5.5	1.02171	3.1	3.0	9.6	1.03848	5.4	5.3
1.5	1.00583	0.85	0.8	5.6	1.02211	3.2	3.1	9.7	1.03889	5.5	5.4
1.6	1.00622	0.9	0.9	5.7	1.02252	3.2	3.2	9.8	1.03931	5.55	5.4
1.7	1.00662	1.0	0.9	5.8	1.02292	3.3	3.2	9.9	1.03972	5.6	5.5
1.8	1.00701	1.0	1.0	5.9	1.02333	3.35	3.3	10.0	1.04014	5.7	5.5
1.9	1.00740	1.1	1.05	6.0	1.02373	3.4	3.3	10.1	1.04055	5.7	5.6
2.0	1.00779	1.1	1.1	6.1	1.02413	3.5	3.4	10.2	1.04097	5.8	5.7
2.1	1.00818	1.2	1.2	6.2	1.02454	3.5	3.4	10.3	1.04139	5.8	5.7
2.2	1.00858	1.2	1.2	6.3	1.02494	3.6	3.5	10.4	1.04180	5.9	5.8
2.3	1.00897	1.3	1.3	6.4	1.02535	3.6	3.6	10.5	1.04222	5.9	5.8
2.4	1.00936	1.4	1.3	6.5	1.02575	3.7	3.6	10.6	1.04264	6.0	5.9
2.5	1.00976	1.4	1.4	6.6	1.02616	3.7	3.7	10.7	1.04306	6.1	5.9
2.6	1.01015	1.5	1.4	6.7	1.02657	3.8	3.7	10.8	1.04348	6.1	6.05
2.7	1.01055	1.5	1.5	6.8	1.02697	3.9	3.8	10.9	1.04390	6.2	6.5
2.8	1.01094	1.6	1.55	6.9	1.02738	3.9	3.8	11.0	1.04431	6.2	6.1
2.9	1.01134	1.6	1.6	7.0	1.02779	4.0	3.9	11.1	1.04473	6.3	6.2
3.0	1.01173	1.7	1.7	7.1	1.02819	4.0	3.9	11.2	1.04515	6.3	6.2
3.1	1.01213	1.8	1.7	7.2	1.02860	4.1	4.0	11.3	1.04557	6.4	6.3
3.2	1.01252	1.8	1.8	7.3	1.02901	4.1	4.1	11.4	1.04599	6.5	6.3
3.3	1.01292	1.9	1.8	7.4	1.02942	4.2	4.1	11.5	1.04641	6.5	6.4
3.4	1.01332	1.9	1.9	7.5	1.02983	4.25	4.2	11.6	1.04683	6.6	6.4
3.5	1.01371	2.0	1.9	7.6	1.03024	4.3	4.2	11.7	1.04726	6.6	6.5
3.6	1.01411	2.0	2.0	7.7	1.03064	4.4	4.3	11.8	1.04768	6.7	6.55
3.7	1.01451	2.1	2.0	7.8	1.03105	4.4	4.3	11.9	1.04810	6.7	6.6
3.8	1.01491	2.2	2.1	7.9	1.03146	4.5	4.4	12.0	1.04852	6.8	6.7
3.9	1.01531	2.2	2.2	8.0	1.03187	4.5	4.4	12.1	1.04894	6.8	6.7
4.0	1.01570	2.3	2.2	8.1	1.03228	4.6	4.5	12.2	1.04937	6.9	6.8

¹ For more recent Tables based on that drawn up by the International Commission for Standard Methods of Sugar Analysis, see J. Domke, *Z. Ver. deut. Zuckerind.*, 1912, 52, 302-311; also, *J. Soc. Chem. Ind.*, 1912, 31, 449.

TABLE XXI—*continued.*

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
12.3	1.04979	7.0	6.8	17.9	1.07397	10.1	9.9	23.5	1.09915	13.2	13.0
12.4	1.05021	7.0	6.9	18.0	1.07441	10.1	10.0	23.6	1.09961	13.3	13.0
12.5	1.05064	7.1	6.9	18.1	1.07485	10.2	10.0	23.7	1.10007	13.3	13.1
12.6	1.05106	7.1	7.0	18.2	1.07530	10.3	10.1	23.8	1.10053	13.4	13.15
12.7	1.05149	7.2	7.05	18.3	1.07574	10.3	10.1	23.9	1.10099	13.5	13.2
12.8	1.05191	7.2	7.1	18.4	1.07618	10.4	10.2	24.0	1.10145	13.5	13.3
12.9	1.05233	7.3	7.2	18.5	1.07662	10.4	10.2	24.1	1.10191	13.6	13.3
13.0	1.05276	7.4	7.2	18.6	1.07706	10.5	10.3	24.2	1.10237	13.6	13.4
13.1	1.05318	7.4	7.3	18.7	1.07751	10.5	10.35	24.3	1.10283	13.7	13.4
13.2	1.05361	7.5	7.3	18.8	1.07795	10.6	10.4	24.4	1.10329	13.7	13.5
13.3	1.05404	7.5	7.4	18.9	1.07839	10.6	10.5	24.5	1.10375	13.8	13.5
13.4	1.05446	7.6	7.4	19.0	1.07884	10.7	10.5	24.6	1.10421	13.8	13.6
13.5	1.05489	7.6	7.5	19.1	1.07928	10.8	10.6	24.7	1.10468	13.9	13.6
13.6	1.05532	7.7	7.5	19.2	1.07973	10.8	10.6	24.8	1.10514	14.0	13.7
13.7	1.05574	7.75	7.6	19.3	1.08017	10.9	10.7	24.9	1.10560	14.0	13.75
13.8	1.05617	7.8	7.65	19.4	1.08062	10.9	10.7	25.0	1.10607	14.1	13.8
13.9	1.05660	7.9	7.7	19.5	1.08106	11.0	10.8	25.1	1.10653	14.1	13.9
14.0	1.05703	7.9	7.8	19.6	1.08151	11.1	10.85	25.2	1.10700	14.2	13.9
14.1	1.05746	8.0	7.8	19.7	1.08196	11.1	10.9	25.3	1.10746	14.2	14.0
14.2	1.05789	8.0	7.9	19.8	1.08240	11.2	11.0	25.4	1.10793	14.3	14.0
14.3	1.05831	8.1	7.9	19.9	1.08285	11.2	11.0	25.5	1.10839	14.3	14.1
14.4	1.05874	8.1	8.0	20.0	1.08329	11.3	11.1	25.6	1.10886	14.4	14.1
14.5	1.05917	8.2	8.0	20.1	1.08374	11.3	11.1	25.7	1.10932	14.5	14.2
14.6	1.05960	8.3	8.1	20.2	1.08419	11.4	11.2	25.8	1.10979	14.5	14.2
14.7	1.06003	8.3	8.15	20.3	1.08464	11.5	11.2	25.9	1.11026	14.6	14.3
14.8	1.06047	8.4	8.2	20.4	1.08509	11.5	11.3	26.0	1.11072	14.6	14.35
14.9	1.06090	8.4	8.3	20.5	1.08553	11.6	11.3	26.1	1.11119	14.7	14.4
15.0	1.06133	8.5	8.3	20.6	1.08599	11.6	11.4	26.2	1.11166	14.7	14.5
15.1	1.06176	8.5	8.4	20.7	1.08643	11.7	11.45	26.3	1.11213	14.8	14.5
15.2	1.06219	8.55	8.4	20.8	1.08688	11.7	11.5	26.4	1.11259	14.85	14.6
15.3	1.06262	8.6	8.5	20.9	1.08733	11.8	11.6	26.5	1.11306	14.9	14.6
15.4	1.06306	8.7	8.5	21.0	1.08778	11.8	11.6	26.6	1.11353	15.0	14.7
15.5	1.06349	8.8	8.6	21.1	1.08824	11.9	11.7	26.7	1.11400	15.0	14.7
15.6	1.06392	8.8	8.65	21.2	1.08869	11.95	11.7	26.8	1.11447	15.1	14.8
15.7	1.06436	8.9	8.7	21.3	1.08914	12.0	11.8	26.9	1.11494	15.1	14.8
15.8	1.06479	8.9	8.8	21.4	1.08959	12.0	11.8	27.0	1.11541	15.2	14.9
15.9	1.06522	9.0	8.8	21.5	1.09004	12.1	11.9	27.1	1.11588	15.2	14.9
16.0	1.06566	9.0	8.9	21.6	1.09049	12.1	11.95	27.2	1.11635	15.3	15.0
16.1	1.06609	9.1	8.9	21.7	1.09095	12.2	12.0	27.3	1.11682	15.3	15.1
16.2	1.06653	9.2	9.0	21.8	1.09140	12.3	12.05	27.4	1.11729	15.4	15.1
16.3	1.06696	9.2	9.0	21.9	1.09185	12.3	12.1	27.5	1.11776	15.5	15.2
16.4	1.06740	9.3	9.1	22.0	1.09231	12.4	12.2	27.6	1.11824	15.5	15.2
16.5	1.06783	9.3	9.1	22.1	1.09276	12.5	12.2	27.7	1.11871	15.6	15.3
16.6	1.06827	9.4	9.2	22.2	1.09321	12.5	12.3	27.8	1.11918	15.6	15.3
16.7	1.06871	9.4	9.25	22.3	1.09367	12.6	12.3	27.9	1.11965	15.7	15.4
16.8	1.06914	9.5	9.3	22.4	1.09412	12.6	12.4	28.0	1.12013	15.7	15.4
16.9	1.06958	9.5	9.4	22.5	1.09458	12.7	12.4	28.1	1.12060	15.8	15.5
17.0	1.07002	9.6	9.4	22.6	1.09503	12.7	12.5	28.2	1.12107	15.8	15.55
17.1	1.07046	9.7	9.5	22.7	1.09549	12.8	12.55	28.3	1.12155	15.8	15.6
17.2	1.07090	9.75	9.5	22.8	1.09595	12.85	12.6	28.4	1.12202	16.0	15.7
17.3	1.07133	9.8	9.6	22.9	1.09640	12.9	12.7	28.5	1.12250	16.0	15.7
17.4	1.07177	9.8	9.6	23.0	1.09686	13.0	12.7	28.6	1.12297	16.1	15.8
17.5	1.07221	9.9	9.7	23.1	1.09732	13.0	12.8	28.7	1.12345	16.1	15.9
17.6	1.07265	9.9	9.7	23.2	1.09777	13.1	12.8	28.8	1.12393	16.2	15.9
17.7	1.07309	10.0	9.8	23.3	1.09823	13.1	12.9	28.9	1.12440	16.2	15.9
17.8	1.07353	10.0	9.9	23.4	1.09869	13.2	12.9	29.0	1.12488	16.3	16.0

TABLE XXI—*continued.*

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
29.1	1.12536	16.3	16.0	34.7	1.15262	19.4	19.1	40.3	1.18098	22.5	22.1
29.2	1.12583	16.4	16.1	34.8	1.15312	19.5	19.1	40.4	1.18150	22.5	22.1
29.3	1.12631	16.5	16.1	34.9	1.15362	19.5	19.2	40.5	1.18201	22.6	22.2
29.4	1.12679	16.5	16.2	35.0	1.15411	19.6	19.2	40.6	1.18253	22.6	22.2
29.5	1.12727	16.6	16.25	35.1	1.15461	19.65	19.3	40.7	1.18305	22.7	22.3
29.6	1.12775	16.6	16.3	35.2	1.15511	19.7	19.3	40.8	1.18357	22.8	22.3
29.7	1.12823	16.7	16.4	35.3	1.15561	19.8	19.4	40.9	1.18408	22.8	22.4
29.8	1.12871	16.7	16.4	35.4	1.15611	19.8	19.4	41.0	1.18460	22.9	22.4
29.9	1.12919	16.8	16.5	35.5	1.15661	19.9	19.5	41.1	1.18512	22.9	22.5
30.0	1.12967	16.8	16.5	35.6	1.15710	19.9	19.55	41.2	1.18564	23.0	22.5
30.1	1.13015	16.9	16.6	35.7	1.15760	20.0	19.6	41.3	1.18616	23.0	22.6
30.2	1.13063	16.95	16.6	35.8	1.15810	20.0	19.65	41.4	1.18668	23.1	22.65
30.3	1.13111	17.0	16.7	35.9	1.15861	20.1	19.7	41.5	1.18720	23.1	22.7
30.4	1.13159	17.1	16.7	36.0	1.15911	20.1	19.8	41.6	1.18772	23.2	22.75
30.5	1.13207	17.1	16.8	36.1	1.15961	20.2	19.8	41.7	1.18824	23.25	22.8
30.6	1.13255	17.2	16.85	36.2	1.16011	20.25	19.9	41.8	1.18877	23.3	22.9
30.7	1.13304	17.2	16.9	36.3	1.16061	20.3	19.9	41.9	1.18929	23.4	22.9
30.8	1.13352	17.3	17.0	36.4	1.16111	20.4	20.0	42.0	1.18981	23.4	23.0
30.9	1.13400	17.3	17.0	36.5	1.16162	20.4	20.0	42.1	1.19033	23.5	23.0
31.0	1.13449	17.4	17.1	36.6	1.16212	20.5	20.1	42.2	1.19086	23.5	23.1
31.1	1.13497	17.45	17.1	36.7	1.16262	20.5	20.1	42.3	1.19138	23.6	23.1
31.2	1.13545	17.5	17.2	36.8	1.16313	20.6	20.2	42.4	1.19190	23.6	23.2
31.3	1.13594	17.6	17.2	36.9	1.16363	20.6	20.2	42.5	1.19243	23.7	23.2
31.4	1.13642	17.6	17.3	37.0	1.16413	20.7	20.3	42.6	1.19295	23.7	23.3
31.5	1.13691	17.7	17.3	37.1	1.16464	20.7	20.35	42.7	1.19348	23.8	23.3
31.6	1.13740	17.7	17.4	37.2	1.16514	20.8	20.4	42.8	1.19400	23.8	23.4
31.7	1.13788	17.8	17.4	37.3	1.16565	20.9	20.5	42.9	1.19453	23.9	23.45
31.8	1.13837	17.8	17.5	37.4	1.16616	20.9	20.5	43.0	1.19505	23.95	23.5
31.9	1.13885	17.9	17.55	37.5	1.16666	21.0	20.6	43.1	1.19558	24.0	23.55
32.0	1.13934	17.95	17.6	37.6	1.16717	21.0	20.6	43.2	1.19611	24.1	23.6
32.1	1.13983	18.0	17.7	37.7	1.16768	21.1	20.7	43.3	1.19663	24.1	23.7
32.2	1.14032	18.0	17.7	37.8	1.16818	21.1	20.7	43.4	1.19716	24.2	23.7
32.3	1.14081	18.1	17.8	37.9	1.16869	21.2	20.8	43.5	1.19769	24.2	23.8
32.4	1.14129	18.2	17.8	38.0	1.16920	21.2	20.8	43.6	1.19822	24.3	23.8
32.5	1.14178	18.2	17.9	38.1	1.16971	21.3	20.9	43.7	1.19875	24.3	23.9
32.6	1.14227	18.3	17.9	38.2	1.17022	21.35	20.9	43.8	1.19927	24.4	23.9
32.7	1.14276	18.3	18.0	38.3	1.17072	21.4	21.0	43.9	1.19980	24.4	24.0
32.8	1.14325	18.4	18.0	38.4	1.17123	21.5	21.05	44.0	1.20033	24.5	24.0
32.9	1.14374	18.4	18.1	38.5	1.17174	21.5	21.1	44.1	1.20086	24.55	24.1
33.0	1.14423	18.5	18.15	38.6	1.17225	21.6	21.15	44.2	1.20139	24.6	24.1
33.1	1.14472	18.55	18.2	38.7	1.17276	21.6	21.2	44.3	1.20192	24.65	24.2
33.2	1.14521	18.6	18.25	38.8	1.17327	21.7	21.3	44.4	1.20245	24.7	24.2
33.3	1.14570	18.7	18.3	38.9	1.17379	21.7	21.3	44.5	1.20299	24.8	24.3
33.4	1.14620	18.7	18.4	39.0	1.17430	21.8	21.4	44.6	1.20352	24.8	24.35
33.5	1.14669	18.8	18.4	39.1	1.17481	21.8	21.4	44.7	1.20405	24.9	24.4
33.6	1.14718	18.8	18.5	39.2	1.17532	21.9	21.5	44.8	1.20458	24.9	24.45
33.7	1.14767	18.9	18.5	39.3	1.17583	21.9	21.5	44.9	1.20512	25.0	24.5
33.8	1.14817	18.9	18.6	39.4	1.17635	22.0	21.6	45.0	1.20565	25.0	24.6
33.9	1.14866	19.0	18.6	39.5	1.17686	22.05	21.6	45.1	1.20618	25.1	24.6
34.0	1.14915	19.05	18.7	39.6	1.17737	22.1	21.7	45.2	1.20672	25.1	24.7
34.1	1.14965	19.1	18.7	39.7	1.17789	22.2	21.7	45.3	1.20725	25.2	24.7
34.2	1.15014	19.2	18.8	39.8	1.17840	22.2	21.8	45.4	1.20779	25.2	24.8
34.3	1.15064	19.2	18.85	39.9	1.17892	22.3	21.85	45.5	1.20832	25.3	24.8
34.4	1.15113	19.3	18.9	40.0	1.17943	22.3	21.9	45.6	1.20886	25.4	24.9
34.5	1.15163	19.3	18.95	40.1	1.17995	22.4	22.0	45.7	1.20939	25.4	24.9
34.6	1.15213	19.4	19.0	40.2	1.18046	22.4	22.0	45.8	1.20993	25.5	25.0

TABLE XXI—*continued.*

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
45.9	1.21046	25.5	25.0	51.5	1.24111	28.5	28.0	57.1	1.27293	31.5	30.9
46.0	1.21100	25.6	25.1	51.6	1.24166	28.6	28.0	57.2	1.27351	31.5	30.9
46.1	1.21154	25.6	25.1	51.7	1.24222	28.6	28.1	57.3	1.27409	31.6	31.0
46.2	1.21208	25.7	25.2	51.8	1.24278	28.7	28.1	57.4	1.27464	31.6	31.0
46.3	1.21261	25.7	25.2	51.9	1.24334	28.7	28.2	57.5	1.27525	31.7	31.1
46.4	1.21315	25.8	25.3	52.0	1.24390	28.8	28.2	57.6	1.27583	31.7	31.1
46.5	1.21369	25.8	25.35	52.1	1.24446	28.8	28.3	57.7	1.27641	31.8	31.2
46.6	1.21423	25.9	25.4	52.2	1.24502	28.9	28.3	57.8	1.27699	31.8	31.2
46.7	1.21477	25.95	25.45	52.3	1.24558	28.9	28.4	57.9	1.27758	31.9	31.3
46.8	1.21531	26.0	25.5	52.4	1.24614	29.0	28.4	58.0	1.27816	31.9	31.3
46.9	1.21585	26.1	25.6	52.5	1.24670	29.0	28.5	58.1	1.27874	32.0	31.4
47.0	1.21639	26.1	25.6	52.6	1.24726	29.1	28.5	58.2	1.27932	32.0	31.4
47.1	1.21693	26.2	25.7	52.7	1.24782	29.15	28.6	58.3	1.27991	32.1	31.5
47.2	1.21747	26.2	25.7	52.8	1.24839	29.2	28.65	58.4	1.28049	32.15	31.5
47.3	1.21802	26.3	25.8	52.9	1.24895	29.2	28.7	58.5	1.28107	32.2	31.6
47.4	1.21856	26.3	25.8	53.0	1.24951	29.3	28.75	58.6	1.28166	32.3	31.6
47.5	1.21910	26.4	25.9	53.1	1.25008	29.4	28.8	58.7	1.28224	32.3	31.7
47.6	1.21964	26.4	25.9	53.2	1.25064	29.4	28.85	58.8	1.28283	32.4	31.7
47.7	1.22019	26.5	26.0	53.3	1.25120	29.5	28.9	58.9	1.28342	32.4	31.8
47.8	1.22073	26.5	26.0	53.4	1.25177	29.5	28.9	59.0	1.28400	32.5	31.85
47.9	1.22127	26.6	26.1	53.5	1.25233	29.6	29.0	59.1	1.28459	32.5	31.9
48.0	1.22182	26.6	26.1	53.6	1.25290	29.6	29.1	59.2	1.28518	32.6	31.95
48.1	1.22236	26.7	26.2	53.7	1.25347	29.7	29.1	59.3	1.28576	32.6	32.0
48.2	1.22291	26.75	26.2	53.8	1.25403	29.7	29.2	59.4	1.28635	32.7	32.05
48.3	1.22345	26.8	26.3	53.9	1.25460	29.8	29.2	59.5	1.28694	32.7	32.1
48.4	1.22400	26.9	26.35	54.0	1.25517	29.8	29.3	59.6	1.28753	32.8	32.15
48.5	1.22455	26.9	26.4	54.1	1.25573	29.9	29.3	59.7	1.28812	32.8	32.2
48.6	1.22509	27.0	26.45	54.2	1.25630	29.9	29.4	59.8	1.28871	32.9	32.3
48.7	1.22564	27.0	26.5	54.3	1.25687	30.0	29.4	59.9	1.28930	32.9	32.3
48.8	1.22619	27.1	26.6	54.4	1.25744	30.05	29.5	60.0	1.28989	33.0	32.4
48.9	1.22673	27.1	26.6	54.5	1.25801	30.1	29.5	60.1	1.29048	33.0	32.4
49.0	1.22728	27.2	26.7	54.6	1.25857	30.2	29.6	60.2	1.29107	33.1	32.5
49.1	1.22783	27.2	26.7	54.7	1.25914	30.2	29.6	60.3	1.29166	33.1	32.5
49.2	1.22838	27.3	26.8	54.8	1.25971	30.3	29.7	60.4	1.29225	33.2	32.6
49.3	1.22893	27.3	26.8	54.9	1.26028	30.3	29.7	60.5	1.29284	33.2	32.6
49.4	1.22948	27.4	26.9	55.0	1.26086	30.4	29.8	60.6	1.29343	33.3	32.7
49.5	1.23003	27.4	26.9	55.1	1.26143	30.4	29.8	60.7	1.29403	33.35	32.7
49.6	1.23058	27.5	27.0	55.2	1.26200	30.5	29.9	60.8	1.29462	33.4	32.8
49.7	1.23113	27.6	27.0	55.3	1.26257	30.5	29.9	60.9	1.29521	33.45	32.8
49.8	1.23168	27.6	27.1	55.4	1.26314	30.6	30.0	61.0	1.29581	33.5	32.9
49.9	1.23223	27.7	27.1	55.5	1.26372	30.6	30.05	61.1	1.29640	33.6	32.9
50.0	1.23278	27.7	27.2	55.6	1.26429	30.7	30.1	61.2	1.29700	33.6	33.0
50.1	1.23334	27.8	27.2	55.7	1.26486	30.7	30.15	61.3	1.29759	33.7	33.0
50.2	1.23389	27.8	27.3	55.8	1.26544	30.8	30.2	61.4	1.29819	33.7	33.1
50.3	1.23444	27.9	27.3	55.9	1.26601	30.8	30.25	61.5	1.29878	33.8	33.1
50.4	1.23499	27.9	27.4	56.0	1.26658	30.9	30.3	61.6	1.29938	33.8	33.2
50.5	1.23555	28.0	27.45	56.1	1.26716	30.9	30.4	61.7	1.29998	33.9	33.2
50.6	1.23610	28.0	27.5	56.2	1.26773	31.0	30.4	61.8	1.30057	33.9	33.3
50.7	1.23666	28.1	27.55	56.3	1.26831	31.05	30.5	61.9	1.30117	34.0	33.3
50.8	1.23721	28.1	27.6	56.4	1.26889	31.1	30.5	62.0	1.30177	34.0	33.4
50.9	1.23777	28.2	27.7	56.5	1.26946	31.2	30.6	62.1	1.30237	34.1	33.4
51.0	1.23832	28.2	27.7	56.6	1.27004	31.2	30.6	62.2	1.30297	34.1	33.5
51.1	1.23888	28.3	27.8	56.7	1.27062	31.3	30.7	62.3	1.30356	34.2	33.5
51.2	1.23943	28.35	27.8	56.8	1.27120	31.3	30.7	62.4	1.30416	34.2	33.6
51.3	1.23999	28.4	27.9	56.9	1.27177	31.4	30.8	62.5	1.30476	34.3	33.6
51.4	1.24055	28.5	27.9	57.0	1.27235	31.4	30.8	62.6	1.30536	34.3	33.7

TABLE XXI—*continued.*

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
62.7	1.30596	34.4	33.7	68.3	1.34053	37.3	36.6	73.9	1.37575	40.1	39.3
62.8	1.30657	34.4	33.8	68.4	1.34085	37.3	36.6	74.0	1.37639	40.1	39.4
62.9	1.30717	34.5	33.8	68.5	1.34148	37.4	36.7	74.1	1.37704	40.2	39.4
63.0	1.30777	34.5	33.9	68.6	1.34210	37.4	36.7	74.2	1.37768	40.2	39.5
63.1	1.30837	34.6	33.9	68.7	1.34273	37.5	36.8	74.3	1.37833	40.3	39.5
63.2	1.30897	34.6	34.0	68.8	1.34335	37.5	36.8	74.4	1.37898	40.3	39.6
63.3	1.30958	34.7	34.0	68.9	1.34398	37.6	36.9	74.5	1.37962	40.4	39.6
63.4	1.31018	34.7	34.1	69.0	1.34460	37.6	36.9	74.6	1.38027	40.4	39.7
63.5	1.31078	34.8	34.1	69.1	1.34523	37.7	37.0	74.7	1.38092	40.5	39.7
63.6	1.31139	34.85	34.2	69.2	1.34585	37.7	37.0	74.8	1.38157	40.5	39.8
63.7	1.31199	34.9	34.2	69.3	1.34648	37.8	37.1	74.9	1.38222	40.6	39.8
63.8	1.31260	34.95	34.3	69.4	1.34711	37.8	37.1	75.0	1.38287	40.6	39.9
63.9	1.31320	35.0	34.3	69.5	1.34774	37.9	37.2	75.1	1.38352	40.7	39.9
64.0	1.31381	35.1	34.4	69.6	1.34836	37.9	37.2	75.2	1.38417	40.7	40.0
64.1	1.31442	35.1	34.4	69.7	1.34899	38.0	37.3	75.3	1.38482	40.8	40.0
64.2	1.31502	35.2	34.5	69.8	1.34962	38.0	37.3	75.4	1.38547	40.8	40.1
64.3	1.31563	35.2	34.5	69.9	1.35025	38.1	37.4	75.5	1.38612	40.9	40.1
64.4	1.31624	35.3	34.6	70.0	1.35088	38.1	37.4	75.6	1.38677	40.9	40.2
64.5	1.31684	35.3	34.6	70.1	1.35151	38.2	37.5	75.7	1.38743	41.0	40.2
64.6	1.31745	35.4	34.7	70.2	1.35214	38.2	37.5	75.8	1.38808	41.0	40.3
64.7	1.31806	35.4	34.7	70.3	1.35277	38.3	37.6	75.9	1.38873	41.1	40.3
64.8	1.31867	35.5	34.8	70.4	1.35340	38.3	37.6	76.0	1.38939	41.1	40.4
64.9	1.31928	35.5	34.8	70.5	1.35403	38.4	37.7	76.1	1.39004	41.2	40.4
65.0	1.31989	35.6	34.9	70.6	1.35466	38.4	37.7	76.2	1.39070	41.2	40.5
65.1	1.32050	35.6	34.95	70.7	1.35530	38.5	37.8	76.3	1.39135	41.3	40.5
65.2	1.32111	35.7	35.0	70.8	1.35593	38.5	37.8	76.4	1.39201	41.3	40.6
65.3	1.32172	35.7	35.05	70.9	1.35656	38.6	37.9	76.5	1.39266	41.4	40.6
65.4	1.32233	35.8	35.1	71.0	1.35720	38.6	37.9	76.6	1.39332	41.4	40.7
65.5	1.32294	35.8	35.15	71.1	1.35783	38.7	37.9	76.7	1.39397	41.5	40.7
65.6	1.32355	35.9	35.2	71.2	1.35847	38.7	38.0	76.8	1.39463	41.5	40.8
65.7	1.32417	35.9	35.25	71.3	1.35910	38.8	38.0	76.9	1.39529	41.6	40.8
65.8	1.32478	36.0	35.3	71.4	1.35974	38.8	38.1	77.0	1.39595	41.6	40.8
65.9	1.32539	36.0	35.35	71.5	1.36037	38.9	38.1	77.1	1.39660	41.7	40.9
66.0	1.32601	36.1	35.4	71.6	1.36101	38.9	38.2	77.2	1.39726	41.7	40.9
66.1	1.32662	36.1	35.5	71.7	1.36164	39.0	38.2	77.3	1.39792	41.8	41.0
66.2	1.32724	36.2	35.5	71.8	1.36228	39.0	38.3	77.4	1.39858	41.8	41.0
66.3	1.32785	36.2	35.6	71.9	1.36292	39.1	38.3	77.5	1.39924	41.9	41.1
66.4	1.32847	36.3	35.6	72.0	1.36355	39.1	38.4	77.6	1.39990	41.9	41.1
66.5	1.32908	36.3	35.7	72.1	1.36419	39.2	38.4	77.7	1.40056	42.0	41.2
66.6	1.32970	36.4	35.7	72.2	1.36483	39.2	38.5	77.8	1.40122	42.0	41.2
66.7	1.33031	36.4	35.8	72.3	1.36547	39.3	38.5	77.9	1.40188	42.1	41.3
66.8	1.33093	36.5	35.8	72.4	1.36611	39.3	38.6	78.0	1.40254	42.1	41.3
66.9	1.33155	36.5	35.9	72.5	1.36675	39.4	38.6	78.1	1.40321	42.2	41.4
67.0	1.33217	36.6	35.9	72.6	1.36739	39.4	38.7	78.2	1.40387	42.2	41.4
67.1	1.33278	36.6	36.0	72.7	1.36803	39.5	38.7	78.3	1.40453	42.3	41.5
67.2	1.33340	36.7	36.0	72.8	1.36867	39.5	38.8	78.4	1.40520	42.3	41.5
67.3	1.33402	36.75	36.1	72.9	1.36931	39.6	38.8	78.5	1.40586	42.4	41.6
67.4	1.33464	36.8	36.1	73.0	1.36995	39.6	38.9	78.6	1.40652	42.4	41.6
67.5	1.33526	36.85	36.2	73.1	1.37059	39.7	38.9	78.7	1.40719	42.5	41.7
67.6	1.33588	36.9	36.2	73.2	1.37124	39.7	39.0	78.8	1.40785	42.5	41.7
67.7	1.33650	36.95	36.3	73.3	1.37188	39.8	39.0	78.9	1.40852	42.6	41.8
67.8	1.33712	37.0	36.3	73.4	1.37252	39.8	39.1	79.0	1.40918	42.6	41.8
67.9	1.33774	37.0	36.4	73.5	1.37317	39.9	39.1	79.1	1.40985	42.7	41.9
68.0	1.33836	37.1	36.4	73.6	1.37381	39.9	39.2	79.2	1.41052	42.7	41.9
68.1	1.33899	37.1	36.5	73.7	1.37446	40.0	39.2	79.3	1.41118	42.8	42.0
68.2	1.33961	37.2	36.5	73.8	1.37510	40.0	39.3	79.4	1.41185	42.8	42.0

TABLE XXI—*continued.*

Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.		Percentage weight of sugar or degrees Brix.	Specific gravity.	Degrees Baumé.	
		New.	Old.			New.	Old.			New.	Old.
79.5	1.41252	42.9	42.1	84.7	1.44779	45.4	44.5	89.9	1.48416	47.9	47.0
79.6	1.41318	42.9	42.1	84.8	1.44848	45.4	44.6	90.0	1.48486	47.9	47.0
79.7	1.41385	43.0	42.1	84.9	1.44917	45.5	44.6	90.1	1.48558	48.0	47.1
79.8	1.41452	43.0	42.2	85.0	1.44986	45.5	44.7	90.2	1.48629	48.0	47.1
79.9	1.41519	43.1	42.2	85.1	1.45055	45.6	44.7	90.3	1.48700	48.1	47.2
80.0	1.41586	43.1	42.3	85.2	1.45124	45.6	44.8	90.4	1.48771	48.1	47.2
80.1	1.41653	43.2	42.3	85.3	1.45193	45.7	44.8	90.5	1.48842	48.2	47.2
80.2	1.41720	43.2	42.4	85.4	1.45262	45.7	44.9	90.6	1.48913	48.2	47.3
80.3	1.41787	43.2	42.4	85.5	1.45331	45.8	44.9	90.7	1.48985	48.3	47.3
80.4	1.41854	43.3	42.5	85.6	1.45401	45.8	45.0	90.8	1.49056	48.35	47.4
80.5	1.41921	43.3	42.5	85.7	1.45470	45.9	45.0	90.9	1.49127	48.4	47.4
80.6	1.41989	43.4	42.6	85.8	1.45539	45.9	45.0	91.0	1.49199	48.45	47.5
80.7	1.42056	43.45	42.6	85.9	1.45609	46.0	45.1	91.1	1.49270	48.5	47.5
80.8	1.42123	43.5	42.7	86.0	1.45678	46.0	45.1	91.2	1.49342	48.5	47.6
80.9	1.42190	43.55	42.7	86.1	1.45748	46.1	45.2	91.3	1.49413	48.6	47.6
81.0	1.42258	43.6	42.8	86.2	1.45817	46.1	45.2	91.4	1.49485	48.6	47.7
81.1	1.42325	43.65	42.8	86.3	1.45887	46.2	45.3	91.5	1.49556	48.7	47.7
81.2	1.42393	43.7	42.9	86.4	1.45956	46.2	45.3	91.6	1.49628	48.7	47.8
81.3	1.42460	43.7	42.9	86.5	1.46026	46.3	45.4	91.7	1.49700	48.8	47.8
81.4	1.42528	43.8	43.0	86.6	1.46095	46.3	45.4	91.8	1.49771	48.8	47.8
81.5	1.42595	43.8	43.0	86.7	1.46165	46.35	45.5	91.9	1.49843	48.9	47.9
81.6	1.42663	43.9	43.1	86.8	1.46235	46.4	45.5	92.0	1.49915	48.9	47.9
81.7	1.42731	43.9	43.1	86.9	1.46304	46.45	45.6	92.1	1.49987	49.0	48.0
81.8	1.42798	44.0	43.2	87.0	1.46374	46.5	45.6	92.2	1.50058	49.0	48.0
81.9	1.42866	44.0	43.2	87.1	1.46444	46.55	45.7	92.3	1.50130	49.05	48.1
82.0	1.42934	44.1	43.2	87.2	1.46514	46.6	45.7	92.4	1.50202	49.1	48.1
82.1	1.43002	44.1	43.3	87.3	1.46584	46.65	45.8	92.5	1.50274	49.15	48.2
82.2	1.43070	44.2	43.3	87.4	1.46654	46.7	45.8	92.6	1.50346	49.2	48.2
82.3	1.43137	44.2	43.4	87.5	1.46724	46.7	45.8	92.7	1.50419	49.2	48.3
82.4	1.43205	44.3	43.4	87.6	1.46794	46.8	45.9	92.8	1.50491	49.3	48.3
82.5	1.43273	44.3	43.5	87.7	1.46864	46.8	45.9	92.9	1.50563	49.3	48.3
82.6	1.43341	44.4	43.5	87.8	1.46934	46.9	46.0	93.0	1.50635	49.4	48.4
82.7	1.43409	44.4	43.6	87.9	1.47004	46.9	46.0	93.1	1.50707	49.4	48.4
82.8	1.43478	44.5	43.6	88.0	1.47074	47.0	46.1	93.2	1.50779	49.5	48.5
82.9	1.43546	44.5	43.7	88.1	1.47145	47.0	46.1	93.3	1.50852	49.5	48.5
83.0	1.43614	44.6	43.7	88.2	1.47215	47.1	46.2	93.4	1.50924	49.6	48.6
83.1	1.43682	44.6	43.8	88.3	1.47285	47.1	46.2	93.5	1.50996	49.6	48.6
83.2	1.43750	44.7	43.8	88.4	1.47356	47.2	46.3	93.6	1.51069	49.6	48.7
83.3	1.43819	44.7	43.9	88.5	1.47426	47.2	46.3	93.7	1.51141	49.7	48.7
83.4	1.43887	44.8	43.9	88.6	1.47496	47.3	46.4	93.8	1.51214	49.7	48.8
83.5	1.43955	44.8	44.0	88.7	1.47567	47.3	46.4	93.9	1.51286	49.8	48.8
83.6	1.44024	44.9	44.0	88.8	1.47637	47.4	46.5	94.0	1.51359	49.8	48.8
83.7	1.44092	44.9	44.1	88.9	1.47708	47.4	46.5	94.1	1.51431	49.85	48.9
83.8	1.44161	45.0	44.1	89.0	1.47778	47.45	46.5	94.2	1.51504	49.9	48.9
83.9	1.44229	45.0	44.2	89.1	1.47849	47.5	46.6	94.3	1.51577	49.9	49.0
84.0	1.44298	45.1	44.2	89.2	1.47920	47.55	46.6	94.4	1.51649	50.0	49.0
84.1	1.44367	45.1	44.2	89.3	1.47991	47.6	46.7	94.5	1.51722	50.0	49.1
84.2	1.44435	45.15	44.3	89.4	1.48061	47.6	46.7	94.6	1.51795	50.1	49.1
84.3	1.44504	45.2	44.3	89.5	1.48132	47.7	46.8	94.7	1.51868	50.1	49.2
84.4	1.44573	45.25	44.4	89.6	1.48203	47.7	46.8	94.8	1.51941	50.2	49.2
84.5	1.44641	45.3	44.4	89.7	1.48274	47.8	46.9	94.9	1.52014	50.2	49.3
84.6	1.44710	45.35	44.5	89.8	1.48345	47.8	46.9	95.0	1.52087	50.3	49.3

TABLE XXII. (*Text*, p. 578.)

Corrections for Saccharometer readings at different Temperatures
to readings at 17°.5. (Sachs.)

Temperature. ° C.	Degrees Brix of the solution.												
	0	5	10	15	20	25	30	35	40	50	60	70	75
	The reading obtained is to be reduced by:—												
0	0.27	0.30	0.41	0.52	0.62	0.72	0.82	0.92	0.98	1.11	1.22	1.25	1.29
5	0.23	0.30	0.37	0.44	0.52	0.59	0.65	0.72	0.75	0.80	0.88	0.91	0.94
10	0.20	0.26	0.29	0.33	0.36	0.39	0.42	0.45	0.48	0.50	0.54	0.58	0.61
11	0.18	0.23	0.26	0.28	0.31	0.34	0.36	0.39	0.41	0.43	0.47	0.50	0.53
12	0.16	0.20	0.22	0.24	0.26	0.29	0.31	0.33	0.34	0.36	0.40	0.42	0.46
13	0.14	0.18	0.19	0.21	0.22	0.24	0.26	0.27	0.28	0.29	0.33	0.35	0.39
14	0.12	0.15	0.16	0.17	0.18	0.19	0.21	0.22	0.22	0.23	0.26	0.28	0.32
15	0.09	0.11	0.12	0.14	0.14	0.15	0.16	0.17	0.16	0.17	0.19	0.21	0.25
16	0.06	0.07	0.08	0.09	0.10	0.10	0.11	0.12	0.12	0.12	0.14	0.16	0.18
17	0.02	0.02	0.03	0.03	0.03	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.06
	The reading obtained is to be increased by:—												
18	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.02
19	0.06	0.08	0.08	0.09	0.09	0.10	0.10	0.10	0.10	0.10	0.10	0.08	0.06
20	0.11	0.14	0.15	0.17	0.17	0.18	0.18	0.18	0.19	0.19	0.18	0.15	0.11
21	0.16	0.20	0.22	0.24	0.24	0.25	0.25	0.25	0.26	0.26	0.25	0.22	0.18
22	0.21	0.26	0.29	0.31	0.31	0.32	0.32	0.32	0.33	0.34	0.32	0.29	0.25
23	0.27	0.32	0.35	0.37	0.38	0.39	0.39	0.39	0.40	0.42	0.39	0.36	0.33
24	0.32	0.38	0.41	0.43	0.44	0.46	0.46	0.47	0.47	0.50	0.46	0.43	0.40
25	0.37	0.44	0.47	0.49	0.51	0.53	0.54	0.55	0.55	0.58	0.54	0.51	0.48
26	0.43	0.50	0.54	0.56	0.58	0.60	0.61	0.62	0.62	0.66	0.62	0.58	0.55
27	0.49	0.57	0.61	0.63	0.65	0.68	0.68	0.69	0.70	0.74	0.70	0.65	0.62
28	0.56	0.64	0.68	0.70	0.72	0.76	0.76	0.78	0.78	0.82	0.78	0.72	0.70
29	0.63	0.71	0.75	0.78	0.79	0.84	0.84	0.86	0.86	0.90	0.86	0.80	0.78
30	0.70	0.78	0.82	0.87	0.87	0.92	0.92	0.94	0.94	0.98	0.94	0.88	0.86
35	1.10	1.17	1.22	1.24	1.30	1.32	1.33	1.35	1.36	1.39	1.34	1.27	1.25
40	1.50	1.61	1.67	1.71	1.73	1.79	1.79	1.80	1.82	1.83	1.78	1.69	1.65
50	...	2.65	2.71	2.74	2.78	2.80	2.80	2.80	2.80	2.79	2.70	2.56	2.51
60	...	3.87	3.88	3.88	3.88	3.88	3.88	3.88	3.90	3.82	3.70	3.43	3.41
70	...	5.17	5.18	5.20	5.14	5.13	5.10	5.08	5.06	4.90	4.72	4.47	4.35
80	6.62	6.59	6.54	6.46	6.38	6.30	6.26	6.06	5.82	5.50	5.33
90	8.26	8.16	8.06	7.97	7.83	7.71	7.58	7.30	6.96	6.58	6.37
100	10.01	9.87	9.72	9.56	9.39	9.21	9.03	8.64	8.22	7.76	7.42

(Text, pp. 580-585.)

the Soleil-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)

of lead acetate solution.

Percentage Brix and corresponding specific gravity.										Polarimeter degrees.	Per cent. Brix from 12.5 to 20.0.	
5.5. 1.0217.	6.0. 1.0237.	6.5. 1.0258	7.0. 1.0278.	7.5. 1.0298.	8.0. 1.0319.	8.5. 1.0339.	9.0. 1.0360.	9.5. 1.0381.	10.0. 1.0401.		Tenths of a degree.	Per cent. sugar.
0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	1	0.1	0.03
0.56	0.56	0.56	0.56	0.55	0.55	0.55	0.55	0.55	0.55	2	0.2	0.05
0.84	0.84	0.84	0.83	0.83	0.83	0.83	0.83	0.83	0.82	3	0.3	0.08
1.12	1.12	1.11	1.11	1.11	1.11	1.11	1.10	1.10	1.10	4	0.4	0.11
1.40	1.40	1.39	1.39	1.39	1.38	1.38	1.38	1.38	1.37	5	0.5	0.13
1.68	1.67	1.67	1.67	1.66	1.66	1.66	1.66	1.65	1.65	6	0.6	0.16
1.96	1.95	1.95	1.95	1.94	1.94	1.93	1.93	1.93	1.92	7	0.7	0.19
2.24	2.23	2.23	2.22	2.22	2.22	2.21	2.21	2.20	2.20	8	0.8	0.21
2.52	2.51	2.51	2.50	2.50	2.49	2.49	2.48	2.48	2.47	9	0.9	0.24
2.80	2.79	2.79	2.78	2.78	2.77	2.76	2.76	2.75	2.75	10		
3.08	3.07	3.06	3.06	3.05	3.05	3.04	3.03	3.03	3.02	11		
3.36	3.35	3.34	3.34	3.33	3.32	3.32	3.31	3.30	3.30	12		
3.64	3.63	3.62	3.61	3.61	3.60	3.59	3.59	3.58	3.57	13		
3.92	3.91	3.90	3.89	3.88	3.88	3.87	3.86	3.85	3.85	14		
4.19	4.19	4.18	4.17	4.16	4.15	4.15	4.14	4.13	4.12	15	Per cent. Brix from 12.5 to 20.0.	
4.47	4.47	4.46	4.45	4.44	4.43	4.42	4.41	4.40	4.40	16		
4.76	4.75	4.74	4.73	4.72	4.71	4.70	4.69	4.68	4.67	17		
5.03	5.02	5.01	5.00	4.99	4.99	4.97	4.97	4.96	4.95	18	Tenths of a degree.	Per cent. sugar.
5.32	5.31	5.29	5.28	5.27	5.26	5.25	5.24	5.23	5.22	19		
	5.58	5.57	5.56	5.55	5.54	5.53	5.52	5.51	5.50	20		
	5.86	5.85	5.84	5.83	5.82	5.81	5.79	5.78	5.77	21	0.1	0.03
		6.13	6.12	6.11	6.09	6.08	6.07	6.06	6.05	22	0.2	0.05
		6.41	6.40	6.38	6.37	6.36	6.35	6.33	6.32	23	0.3	0.08
			6.67	6.66	6.65	6.64	6.62	6.61	6.60	24	0.4	0.11
				6.94	6.93	6.91	6.90	6.89	6.87	25	0.5	0.13
				7.22	7.20	7.19	7.17	7.16	7.15	26	0.6	0.16
					7.48	7.46	7.45	7.44	7.42	27	0.7	0.18
					7.76	7.74	7.73	7.71	7.70	28	0.8	0.21
						8.02	8.00	7.99	7.97	29	0.9	0.23
							8.28	8.26	8.25	30		
							8.55	8.54	8.52	31		
							8.83	8.81	8.80	32		
								9.08	9.07	33		
									9.35	34		
									9.62	35		
										36		
										37		
										38		
										39		

TABLE

Table giving the content of Sucrose in Percentage Weight for
and with regard to the variable Specific

With addition of $\frac{1}{10}$ volume

Per cent. Brix from 0.5 to 12.0.		Polarimeter degrees.	Percentage Brix and corresponding specific gravity.									
Tenths of a degree	Per cent. sugar.		10.5. 1.0422.	11.0. 1.0443.	11.5. 1.0464.	12.0. 1.0485.	12.5. 1.0506.	13.0. 1.0528.	13.5. 1.0549.	14.0. 1.0570.	14.5. 1.0592.	15.0. 1.0613.
0.1	0.03	1	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
0.2	0.06	2	0.55	0.55	0.55	0.55	0.54	0.54	0.54	0.54	0.54	0.54
0.3	0.08	3	0.82	0.82	0.82	0.82	0.82	0.81	0.81	0.81	0.81	0.81
0.4	0.11	4	1.10	1.10	1.09	1.09	1.09	1.09	1.08	1.08	1.08	1.08
0.5	0.14	5	1.37	1.37	1.36	1.36	1.36	1.36	1.35	1.35	1.35	1.35
0.6	0.17	6	1.64	1.64	1.64	1.64	1.63	1.63	1.62	1.62	1.62	1.62
0.7	0.19	7	1.92	1.91	1.91	1.91	1.90	1.90	1.89	1.89	1.89	1.88
0.8	0.22	8	2.19	2.19	2.18	2.18	2.18	2.17	2.17	2.16	2.16	2.15
0.9	0.25	9	2.47	2.46	2.46	2.45	2.45	2.44	2.44	2.43	2.43	2.42
Per cent. Brix from 6.0 to 12.0.		10	2.74	2.74	2.73	2.73	2.72	2.71	2.71	2.70	2.70	2.69
		11	3.02	3.01	3.00	3.00	2.99	2.99	2.98	2.97	2.97	2.96
		12	3.29	3.28	3.28	3.27	3.26	3.26	3.25	3.24	3.24	3.23
		13	3.56	3.56	3.55	3.54	3.54	3.53	3.52	3.51	3.51	3.50
		14	3.84	3.83	3.82	3.82	3.81	3.80	3.79	3.78	3.78	3.77
Tenths of a degree.	Per cent. sugar.	15	4.11	4.11	4.10	4.09	4.08	4.07	4.06	4.06	4.05	4.04
		16	4.39	4.38	4.37	4.36	4.35	4.34	4.33	4.33	4.32	4.31
		17	4.66	4.65	4.64	4.63	4.62	4.62	4.61	4.60	4.59	4.58
		18	4.93	4.93	4.91	4.91	4.90	4.89	4.88	4.87	4.86	4.85
		19	5.21	5.20	5.19	5.18	5.17	5.16	5.15	5.14	5.13	5.12
0.1	0.03	20	5.49	5.47	5.46	5.45	5.44	5.43	5.42	5.41	5.40	5.39
0.2	0.06	21	5.76	5.75	5.74	5.73	5.71	5.70	5.69	5.68	5.67	5.66
0.3	0.08	22	6.03	6.02	6.01	6.00	5.99	5.97	5.96	5.95	5.94	5.93
0.4	0.11	23	6.31	6.30	6.28	6.27	6.26	6.24	6.23	6.22	6.21	6.20
		24	6.58	6.57	6.56	6.54	6.53	6.52	6.50	6.49	6.48	6.46
0.5	0.14	25	6.86	6.84	6.83	6.82	6.80	6.79	6.78	6.76	6.75	6.73
0.6	0.17	26	7.13	7.12	7.10	7.09	7.07	7.06	7.05	7.03	7.02	7.00
0.7	0.19	27	7.41	7.39	7.38	7.36	7.35	7.33	7.32	7.30	7.29	7.27
0.8	0.22	28	7.68	7.66	7.65	7.63	7.62	7.60	7.59	7.57	7.56	7.54
0.9	0.25	29	7.96	7.94	7.92	7.91	7.89	7.87	7.86	7.84	7.83	7.81
		30	8.23	8.21	8.20	8.18	8.16	8.15	8.13	8.11	8.10	8.08
		31	8.50	8.49	8.47	8.45	8.44	8.42	8.40	8.39	8.37	8.35
		32	8.78	8.76	8.74	8.73	8.71	8.69	8.67	8.66	8.64	8.62
		33	9.05	9.03	9.02	9.00	8.98	8.96	8.94	8.93	8.91	8.89
		34	9.33	9.31	9.29	9.27	9.25	9.23	9.22	9.20	9.18	9.16
		35	9.60	9.58	9.56	9.54	9.53	9.51	9.49	9.47	9.45	9.43
		36	9.88	9.86	9.84	9.82	9.80	9.78	9.76	9.74	9.72	9.70
		37	10.15	10.13	10.11	10.09	10.07	10.05	10.03	10.01	9.99	9.97
		38		10.40	10.38	10.36	10.34	10.32	10.30	10.28	10.26	10.24
		39		10.68	10.66	10.64	10.61	10.59	10.57	10.55	10.53	10.51

XXIII—continued.

the Soleil-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)
of lead acetate solution.

Percentage Brix and corresponding specific gravity.										Polarimeter degrees.	Per cent. Brix from 12.5 to 20.0.	
15.5. 1.0635.	16.0. 1.0657.	16.5. 1.0678.	17.0. 1.0700.	17.5. 1.0722.	18.0. 1.0744.	18.5. 1.0766.	19.0. 1.0788.	19.5 1.0811.	20.0. 1.0833.		Tenths of a degree.	Per cent. sugar.
0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.26	1	0.1	0.03
0.54	0.54	0.54	0.53	0.53	0.53	0.53	0.53	0.53	0.53	2	0.2	0.05
0.81	0.80	0.80	0.80	0.80	0.80	0.80	0.79	0.79	0.79	3	0.3	0.08
1.08	1.07	1.07	1.07	1.07	1.06	1.06	1.06	1.06	1.06	4	0.4	0.11
1.34	1.34	1.34	1.34	1.33	1.33	1.33	1.32	1.32	1.32	5	0.5	0.13
1.61	1.61	1.61	1.60	1.60	1.60	1.59	1.59	1.59	1.58	6	0.6	0.16
1.88	1.88	1.87	1.87	1.86	1.86	1.86	1.85	1.85	1.85	7	0.7	0.19
2.15	2.15	2.14	2.14	2.13	2.13	2.12	2.12	2.12	2.11	8	0.8	0.21
2.42	2.41	2.41	2.40	2.40	2.39	2.39	2.38	2.38	2.37	9	0.9	0.24
2.69	2.68	2.68	2.67	2.67	2.66	2.65	2.65	2.64	2.64	10		
2.95	2.95	2.94	2.94	2.93	2.92	2.92	2.91	2.91	2.90	11		
3.22	3.22	3.21	3.20	3.20	3.19	3.18	3.18	3.17	3.17	12		
3.49	3.49	3.48	3.47	3.46	3.46	3.45	3.44	3.44	3.43	13		
3.76	3.75	3.75	3.74	3.73	3.72	3.72	3.71	3.70	3.69	14		
4.03	4.02	4.02	4.01	4.00	3.99	3.98	3.97	3.97	3.96	15	Per cent. Brix from 12.5 to 20.0.	
4.30	4.29	4.28	4.27	4.26	4.26	4.25	4.24	4.23	4.22	16		
4.57	4.56	4.55	4.54	4.53	4.52	4.51	4.50	4.49	4.48	17		
4.84	4.83	4.82	4.81	4.80	4.79	4.78	4.77	4.76	4.75	18	Tenths of a degree.	Per cent. sugar.
5.11	5.10	5.09	5.08	5.06	5.05	5.04	5.03	5.02	5.01	19		
5.38	5.36	5.35	5.34	5.33	5.32	5.31	5.30	5.29	5.28	20		
5.65	5.63	5.62	5.61	5.60	5.59	5.58	5.56	5.55	5.54	21	0.1	0.03
5.91	5.90	5.89	5.88	5.87	5.85	5.84	5.83	5.82	5.80	22	0.2	0.05
6.18	6.17	6.16	6.14	6.13	6.12	6.11	6.09	6.08	6.07	23	0.3	0.08
6.45	6.44	6.43	6.41	6.40	6.39	6.37	6.36	6.35	6.33	24	0.4	0.11
6.72	6.71	6.69	6.68	6.67	6.65	6.64	6.63	6.61	6.60	25	0.5	0.13
6.99	6.97	6.96	6.95	6.93	6.92	6.90	6.89	6.88	6.86	26	0.6	0.16
7.26	7.24	7.23	7.21	7.20	7.18	7.17	7.15	7.14	7.13	27	0.7	0.18
7.53	7.51	7.50	7.48	7.47	7.45	7.44	7.42	7.40	7.39	28	0.8	0.21
7.80	7.78	7.77	7.75	7.73	7.72	7.70	7.68	7.67	7.65	29	0.9	0.23
8.06	8.05	8.03	8.02	8.00	7.98	7.97	7.95	7.93	7.92	30		
8.33	8.32	8.30	8.28	8.27	8.25	8.23	8.21	8.20	8.18	31		
8.60	8.58	8.57	8.55	8.53	8.51	8.50	8.48	8.46	8.45	32		
8.87	8.85	8.84	8.82	8.80	8.78	8.76	8.75	8.73	8.71	33		
9.14	9.12	9.10	9.09	9.07	9.05	9.03	9.01	8.99	8.97	34		
9.41	9.39	9.37	9.35	9.34	9.31	9.30	9.28	9.26	9.24	35		
9.68	9.66	9.64	9.62	9.60	9.58	9.56	9.54	9.52	9.50	36		
9.95	9.93	9.91	9.89	9.87	9.85	9.83	9.81	9.79	9.77	37		
10.22	10.20	10.18	10.15	10.13	10.11	10.09	10.07	10.05	10.03	38		
10.49	10.46	10.44	10.42	10.40	10.38	10.36	10.34	10.32	10.29	39		

XXIII—continued.

the Soliel-Ventzke-Scheibler Polarimeter for observed Densities
Rotatory Power of Sugar. (M. Schmitz.)

of lead acetate solution.

Percentage Brix and corresponding specific gravity.													Polarimeter degrees.	Per cent. Brix from 23·0 to 24·0.	
18·0 1·0744	18·5 1·0766	19·0 1·0788	19·5 1·0811	20·0 1·0833	20·5 1·0855	21·0 1·0878	21·5 1·0900	22·0 1·0923	22·5 1·0946	23·0 1·0969	23·5 1·0992	24·0 1·1015		Tenths of a degree.	Per cent. sugar.
10·64	10·62	10·60	10·58	10·56	10·54	10·52	10·49	10·47	10·45	10·43	10·41	10·38	40		
10·91	10·89	10·87	10·85	10·82	10·80	10·78	10·76	10·74	10·71	10·69	10·67	10·65	41	0·1	0·03
11·18	11·16	11·13	11·11	11·09	11·07	11·04	11·02	11·00	10·97	10·95	10·93	10·90	42	0·2	0·05
11·45	11·42	11·40	11·38	11·35	11·33	11·31	11·28	11·26	11·24	11·21	11·19	11·17	43	0·3	0·08
11·71	11·69	11·66	11·64	11·62	11·59	11·57	11·55	11·52	11·50	11·47	11·45	11·42	44	0·4	0·10
11·98	11·96	11·93	11·91	11·88	11·86	11·83	11·81	11·78	11·76	11·73	11·71	11·69	45	0·5	0·13
12·25	12·22	12·20	12·17	12·15	12·12	12·09	12·07	12·05	12·02	12·00	11·97	11·94	46	0·6	0·16
12·51	12·49	12·46	12·44	12·41	12·39	12·36	12·33	12·31	12·28	12·26	12·23	12·21	47	0·7	0·18
12·78	12·75	12·73	12·70	12·67	12·65	12·62	12·60	12·57	12·54	12·52	12·49	12·47	48	0·8	0·21
13·05	13·02	12·99	12·97	12·94	12·91	12·88	12·86	12·83	12·81	12·78	12·75	12·73	49	0·9	0·23
13·31	13·29	13·26	13·23	13·20	13·18	13·15	13·12	13·09	13·07	13·04	13·01	12·99	50		
13·58	13·55	13·52	13·50	13·47	13·44	13·41	13·39	13·36	13·33	13·30	13·27	13·25	51		
13·85	13·82	13·79	13·76	13·73	13·70	13·68	13·65	13·62	13·59	13·56	13·53	13·51	52		
14·11	14·08	14·05	14·03	14·00	13·97	13·94	13·91	13·88	13·85	13·82	13·79	13·77	53		
14·38	14·35	14·32	14·29	14·26	14·23	14·20	14·17	14·14	14·11	14·08	14·04	14·02	54		
14·65	14·62	14·59	14·56	14·53	14·50	14·47	14·44	14·41	14·38	14·35	14·32	14·29	55		
14·91	14·88	14·85	14·82	14·79	14·76	14·73	14·70	14·67	14·64	14·61	14·58	14·55	56		
15·18	15·15	15·12	15·09	15·06	15·02	14·99	14·96	14·93	14·90	14·87	14·84	14·81	57		
15·45	15·42	15·38	15·35	15·32	15·29	15·26	15·23	15·19	15·16	15·13	15·10	15·07	58		
15·71	15·68	15·65	15·62	15·58	15·55	15·52	15·49	15·46	15·42	15·39	15·36	15·33	59		
15·98	15·95	15·92	15·88	15·85	15·82	15·78	15·75	15·72	15·69	15·65	15·62	15·59	60		
16·25	16·21	16·18	16·15	16·11	16·08	16·05	16·01	15·98	15·95	15·91	15·88	15·85	61	0·1	0·03
16·52	16·48	16·45	16·41	16·38	16·35	16·31	16·28	16·24	16·21	16·18	16·14	16·11	62	0·2	0·05
16·78	16·75	16·71	16·68	16·64	16·61	16·57	16·54	16·51	16·47	16·44	16·40	16·37	63	0·3	0·08
17·05	17·01	16·98	16·94	16·91	16·87	16·84	16·80	16·77	16·73	16·70	16·66	16·63	64	0·4	0·10
17·32	17·28	17·24	17·21	17·17	17·14	17·10	17·07	17·03	17·00	16·96	16·92	16·89	65	0·5	0·13
	17·55	17·51	17·47	17·44	17·40	17·37	17·33	17·29	17·26	17·22	17·19	17·15	66	0·6	0·16
	17·81	17·78	17·74	17·70	17·67	17·63	17·59	17·56	17·52	17·48	17·45	17·41	67	0·7	0·18
		18·04	18·00	17·97	17·93	17·89	17·86	17·82	17·78	17·74	17·71	17·67	68	0·8	0·21
		18·31	18·27	18·23	18·19	18·16	18·12	18·08	18·04	18·00	17·97	17·93	69	0·9	0·23
			18·53	18·50	18·46	18·42	18·38	18·35	18·31	18·27	18·23	18·19	70		
				18·76	18·72	18·68	18·65	18·61	18·57	18·53	18·49	18·45	71		
				19·03	18·99	18·95	18·91	18·87	18·83	18·79	18·75	18·71	72		
					19·25	19·21	19·17	19·13	19·09	19·05	19·01	18·97	73		
					19·52	19·48	19·44	19·40	19·35	19·31	19·27	19·23	74		
						19·78	19·74	19·70	19·66	19·62	19·57	19·53	75		
							20·00	19·96	19·92	19·88	19·84	19·80	76		
							20·27	20·22	20·18	20·14	20·10	20·06	77		
								20·49	20·45	20·40	20·36	20·32	78		
								20·75	20·71	20·66	20·62	20·58	79		
									20·97	20·93	20·88	20·84	80		

TABLE XXIV. (*Text*, p. 586.)

Table giving the Percentage of Sugar corresponding to the Polarimeter Readings for solutions clarified with $\frac{1}{10}$ volume of basic lead acetate. (Neumann.)

Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.	Polarisation degrees.	Per cent. sugar.
1	0·29	26	7·22	51	13·75	76	19·90
2	0·57	27	7·48	52	14·01	77	20·14
3	0·86	28	7·75	53	14·26	78	20·37
4	1·14	29	8·02	54	14·51	79	20·61
5	1·42	30	8·29	55	14·76	80	20·84
6	1·71	31	8·56	56	15·01	81	21·07
7	1·99	32	8·82	57	15·26	82	21·30
8	2·27	33	9·09	58	15·51	83	21·53
9	2·55	34	9·35	59	15·76	84	21·77
10	2·83	35	9·61	60	16·01	85	22·01
11	3·11	36	9·87	61	16·26	86	22·25
12	3·39	37	10·14	62	16·51	87	22·49
13	3·67	38	10·40	63	16·76	88	22·73
14	3·94	39	10·66	64	17·01	89	22·97
15	4·22	40	10·92	65	17·26	90	23·21
16	4·49	41	11·18	66	17·51	91	23·44
17	4·76	42	11·44	67	17·76	92	23·67
18	5·04	43	11·70	68	18·00	93	23·90
19	5·31	44	11·96	69	18·24	94	24·13
20	5·59	45	12·22	70	18·48	95	24·36
21	5·86	46	12·48	71	18·72	96	24·59
22	6·13	47	12·74	72	18·96	97	24·82
23	6·41	48	12·99	73	19·19	98	25·05
24	6·68	49	13·24	74	19·43	99	25·28
25	6·95	50	13·49	75	19·68	100	25·51

Fractions of a degree.	Readings in whole degrees.		
	1 to 30.	31 to 65.	66 to 100.
0·1	0·03	0·03	0·02
0·2	0·05	0·05	0·05
0·3	0·08	0·08	0·07
0·4	0·11	0·10	0·09
0·5	0·14	0·13	0·12
0·6	0·16	0·15	0·14
0·7	0·19	0·18	0·17
0·8	0·22	0·20	0·19
0·9	0·25	0·23	0·21

TABLE XXV. (*Text*, pp. 599-600.)

Table for the Calculation of the Inversion Polarisation.

A. *Temperature Corrections according to Hammerschmidt.*

$$I_{20} = I_t + 0.0038K(20 - t).$$

K =	134.	132	130	128.	126.	124.	122.	120.	118.	116.	114.	112.	110.	105.	100.	95.	90.
20 - t = 1	0.51	0.50	0.49	0.49	0.48	0.47	0.46	0.46	0.45	0.44	0.43	0.43	0.42	0.40	0.38	0.36	0.34
2	1.02	1.00	0.99	0.97	0.96	0.94	0.93	0.91	0.90	0.88	0.87	0.85	0.84	0.80	0.76	0.72	0.68
3	1.53	1.50	1.48	1.46	1.44	1.41	1.39	1.37	1.35	1.32	1.30	1.28	1.25	1.20	1.14	1.08	1.03
4	2.04	2.01	1.98	1.95	1.92	1.88	1.85	1.82	1.79	1.76	1.73	1.70	1.67	1.60	1.52	1.44	1.37
5	2.55	2.51	2.47	2.43	2.39	2.36	2.32	2.28	2.24	2.20	2.17	2.13	2.09	2.00	1.90	1.81	1.71
6	3.06	3.01	2.96	2.92	2.87	2.83	2.78	2.74	2.69	2.64	2.60	2.55	2.51	2.39	2.28	2.17	2.05
7	3.56	3.51	3.46	3.40	3.35	3.30	3.25	3.19	3.14	3.09	3.03	2.98	2.93	2.79	2.66	2.53	2.39
8	4.07	4.01	3.95	3.89	3.83	3.77	3.71	3.65	3.59	3.53	3.47	3.40	3.34	3.19	3.04	2.89	2.74
9	4.58	4.51	4.45	4.38	4.31	4.24	4.17	4.10	4.04	3.97	3.90	3.83	3.76	3.59	3.42	3.25	3.08

K =	85.	80.	75.	70.	65.	60.	55.	50.	45.	40.	35.	30.	25	20.	15.	10.	5.
20 - t = 1	0.32	0.30	0.29	0.27	0.25	0.23	0.21	0.19	0.17	0.15	0.13	0.11	0.10	0.08	0.06	0.04	0.02
2	0.65	0.61	0.57	0.53	0.49	0.46	0.42	0.38	0.34	0.30	0.27	0.23	0.19	0.15	0.11	0.08	0.04
3	0.97	0.91	0.86	0.80	0.74	0.68	0.63	0.57	0.51	0.46	0.40	0.34	0.29	0.23	0.17	0.11	0.06
4	1.29	1.22	1.14	1.06	0.99	0.91	0.84	0.76	0.68	0.61	0.53	0.46	0.38	0.30	0.23	0.15	0.08
5	1.62	1.52	1.43	1.33	1.24	1.14	1.05	0.95	0.86	0.76	0.67	0.57	0.48	0.38	0.29	0.19	0.10
6	1.94	1.82	1.71	1.60	1.48	1.37	1.25	1.14	1.03	0.91	0.80	0.68	0.57	0.46	0.34	0.23	0.11
7	2.26	2.13	2.00	1.86	1.73	1.60	1.46	1.33	1.20	1.06	0.93	0.80	0.67	0.53	0.40	0.27	0.13
8	2.58	2.43	2.28	2.13	1.98	1.82	1.67	1.52	1.37	1.22	1.06	0.91	0.76	0.61	0.46	0.30	0.15
9	2.91	2.74	2.57	2.39	2.22	2.05	1.88	1.71	1.54	1.37	1.20	1.03	0.86	0.68	0.51	0.34	0.17

B. *Sucrose according to Clerget.*

$S = \frac{100K}{192.66} = 0.75380K.$ $0.75380.$					
1	0.7538	6	4.5228	10	7.5380
2	1.5076	7	5.2766	11	8.2918
3	2.2614	8	6.0304	12	9.0456
4	3.0152	9	6.7842	13	9.7994
5	3.7690				

TABLE XXV—*continued.**C. Sucrose and Raffinose according to the Formulæ.*

$S = \frac{0.5188P - I_{20}}{0.845}$ $= \frac{0.61396P}{0.61396} - \frac{1.18343I_{20}}{1.18343}$				$R = \frac{P - S}{1.85}$ $= 0.5405(P - Z)$		$S = \frac{0.5124P - I_{20}}{0.839}$ $= \frac{0.61073P}{0.61073} - \frac{1.19190I_{20}}{1.19190}$			
1	0.6140	1	1.1834	1	0.541	1	0.6107	1	1.1919
2	1.2279	2	2.3669	2	1.081	2	1.2215	2	2.3838
3	1.8419	3	3.5503	3	1.622	3	1.8322	3	3.5757
4	2.4558	4	4.7337	4	2.162	4	2.4429	4	4.7676
5	3.0698	5	5.9172	5	2.703	5	3.0537	5	5.9595
6	3.6838	6	7.1006	6	3.243	6	3.6644	6	7.1514
7	4.2977	7	8.2840	7	3.784	7	4.2751	7	8.3433
8	4.9117	8	9.4674	8	4.324	8	4.8858	8	9.5352
9	5.5256	9	10.6509	9	4.865	9	5.4966	9	10.7271
10	6.1396	10	11.8343	10	5.405	10	6.1073	10	11.9190

TABLE XXVI. (*Text*, pp. 602-605.)

Table for estimating the Water-Content of Sugar Solutions by means of the Abbé Refractometer. (Main.)

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1·3330	100·0	1·3408	94·5	1·3491	89·0	1·3579	83·5
1·3331	99·9	1·3409	94·4	1·3492	88·9	1·3581	83·4
1·3333	99·8	1·3411	94·3	1·3494	88·8	1·3582	83·3
1·3334	99·7	1·3412	94·2	1·3496	88·7	1·3584	83·2
1·3336	99·6	1·3414	94·1	1·3497	88·6	1·3586	83·1
1·3337	99·5	1·3415	94·0	1·3499	88·5	1·3587	83·0
1·3338	99·4	1·3417	93·9	1·3500	88·4	1·3589	82·9
1·3340	99·3	1·3418	93·8	1·3502	88·3	1·3591	82·8
1·3341	99·2	1·3420	93·7	1·3503	88·2	1·3592	82·7
1·3343	99·1	1·3421	93·6	1·3505	88·1	1·3594	82·6
1·3344	99·0	1·3423	93·5	1·3507	88·0	1·3596	82·5
1·3345	98·9	1·3424	93·4	1·3508	87·9	1·3597	82·4
1·3347	98·8	1·3426	93·3	1·3510	87·8	1·3599	82·3
1·3348	98·7	1·3427	93·2	1·3511	87·7	1·3600	82·2
1·3350	98·6	1·3429	93·1	1·3513	87·6	1·3602	82·1
1·3351	98·5	1·3430	93·0	1·3515	87·5	1·3604	82·0
1·3352	98·4	1·3432	92·9	1·3516	87·4	1·3605	81·9
1·3354	98·3	1·3433	92·8	1·3518	87·3	1·3607	81·8
1·3355	98·2	1·3435	92·7	1·3519	87·2	1·3609	81·7
1·3357	98·1	1·3436	92·6	1·3521	87·1	1·3610	81·6
1·3358	98·0	1·3438	92·5	1·3522	87·0	1·3612	81·5
1·3359	97·9	1·3439	92·4	1·3524	86·9	1·3614	81·4
1·3361	97·8	1·3441	92·3	1·3526	86·8	1·3615	81·3
1·3362	97·7	1·3442	92·2	1·3527	86·7	1·3617	81·2
1·3364	97·6	1·3444	92·1	1·3529	86·6	1·3619	81·1
1·3365	97·5	1·3445	92·0	1·3530	86·5	1·3620	81·0
1·3366	97·4	1·3447	91·9	1·3532	86·4	1·3622	80·9
1·3368	97·3	1·3448	91·8	1·3533	86·3	1·3624	80·8
1·3369	97·2	1·3450	91·7	1·3535	86·2	1·3625	80·7
1·3371	97·1	1·3451	91·6	1·3537	86·1	1·3627	80·6
1·3372	97·0	1·3453	91·5	1·3538	86·0	1·3629	80·5
1·3373	96·9	1·3454	91·4	1·3540	85·9	1·3630	80·4
1·3375	96·8	1·3456	91·3	1·3541	85·8	1·3632	80·3
1·3376	96·7	1·3457	91·2	1·3543	85·7	1·3634	80·2
1·3378	96·6	1·3459	91·1	1·3545	85·6	1·3635	80·1
1·3379	96·5	1·3460	91·0	1·3546	85·5	1·3637	80·0
1·3380	96·4	1·3462	90·9	1·3548	85·4	1·3639	79·9
1·3382	96·3	1·3463	90·8	1·3549	85·3	1·3640	79·8
1·3383	96·2	1·3465	90·7	1·3551	85·2	1·3642	79·7
1·3385	96·1	1·3466	90·6	1·3552	85·1	1·3644	79·6
1·3386	96·0	1·3468	90·5	1·3554	85·0	1·3645	79·5
1·3387	95·9	1·3469	90·4	1·3556	84·9	1·3647	79·4
1·3389	95·8	1·3471	90·3	1·3557	84·8	1·3649	79·3
1·3390	95·7	1·3472	90·2	1·3559	84·7	1·3650	79·2
1·3392	95·6	1·3474	90·1	1·3561	84·6	1·3652	79·1
1·3393	95·5	1·3475	90·0	1·3562	84·5	1·3654	79·0
1·3394	95·4	1·3477	89·9	1·3564	84·4	1·3655	78·9
1·3396	95·3	1·3478	89·8	1·3566	84·3	1·3657	78·8
1·3397	95·2	1·3480	89·7	1·3567	84·2	1·3659	78·7
1·3399	95·1	1·3481	89·6	1·3569	84·1	1·3661	78·6
1·3400	95·0	1·3483	89·5	1·3571	84·0	1·3662	78·5
1·3402	94·9	1·3484	89·4	1·3572	83·9	1·3664	78·4
1·3403	94·8	1·3486	89·3	1·3574	83·8	1·3666	78·3
1·3405	94·7	1·3488	89·2	1·3576	83·7	1·3667	78·2
1·3406	94·6	1·3489	89·1	1·3577	83·6	1·3669	78·1

TABLE XXVI—*continued.*

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1·3671	78·0	1·3773	72·1	1·3880	66·2	1·3991	60·3
1·3672	77·9	1·3774	72·0	1·3882	66·1	1·3993	60·2
1·3674	77·8	1·3776	71·9	1·3884	66·0	1·3995	60·1
1·3676	77·7	1·3778	71·8	1·3885	65·9	1·3997	60·0
1·3677	77·6	1·3780	71·7	1·3887	65·8	1·3999	59·9
1·3679	77·5	1·3782	71·6	1·3889	65·7	1·4001	59·8
1·3681	77·4	1·3783	71·5	1·3891	65·6	1·4003	59·7
1·3682	77·3	1·3785	71·4	1·3893	65·5	1·4005	59·6
1·3684	77·2	1·3787	71·3	1·3895	65·4	1·4007	59·5
1·3686	77·1	1·3789	71·2	1·3896	65·3	1·4009	59·4
1·3687	77·0	1·3790	71·1	1·3898	65·2	1·4011	59·3
1·3689	76·9	1·3792	71·0	1·3900	65·1	1·4013	59·2
1·3691	76·8	1·3794	70·9	1·3902	65·0	1·4015	59·1
1·3692	76·7	1·3796	70·8	1·3904	64·9	1·4017	59·0
1·3694	76·6	1·3798	70·7	1·3906	64·8	1·4019	58·9
1·3696	76·5	1·3799	70·6	1·3908	64·7	1·4021	58·8
1·3697	76·4	1·3801	70·5	1·3910	64·6	1·4022	58·7
1·3699	76·3	1·3803	70·4	1·3912	64·5	1·4024	58·6
1·3701	76·2	1·3805	70·3	1·3913	64·4	1·4026	58·5
1·3703	76·1	1·3806	70·2	1·3915	64·3	1·4028	58·4
1·3704	76·0	1·3808	70·1	1·3917	64·2	1·4030	58·3
1·3706	75·9	1·3810	70·0	1·3919	64·1	1·4032	58·2
1·3708	75·8	1·3812	69·9	1·3921	64·0	1·4034	58·1
1·3709	75·7	1·3814	69·8	1·3923	63·9	1·4036	58·0
1·3711	75·6	1·3816	69·7	1·3925	63·8	1·4038	57·9
1·3713	75·5	1·3817	69·6	1·3927	63·7	1·4040	57·8
1·3714	75·4	1·3819	69·5	1·3929	63·6	1·4042	57·7
1·3716	75·3	1·3821	69·4	1·3931	63·5	1·4044	57·6
1·3718	75·2	1·3823	69·3	1·3932	63·4	1·4046	57·5
1·3719	75·1	1·3825	69·2	1·3934	63·3	1·4048	57·4
1·3721	75·0	1·3827	69·1	1·3936	63·2	1·4050	57·3
1·3723	74·9	1·3828	69·0	1·3938	63·1	1·4052	57·2
1·3725	74·8	1·3830	68·9	1·3940	63·0	1·4054	57·1
1·3726	74·7	1·3832	68·8	1·3942	62·9	1·4056	57·0
1·3728	74·6	1·3834	68·7	1·3944	62·8	1·4058	56·9
1·3730	74·5	1·3836	68·6	1·3946	62·7	1·4060	56·8
1·3732	74·4	1·3838	68·5	1·3948	62·6	1·4062	56·7
1·3733	74·3	1·3839	68·4	1·3950	62·5	1·4064	56·6
1·3735	74·2	1·3841	68·3	1·3951	62·4	1·4066	56·5
1·3737	74·1	1·3843	68·2	1·3953	62·3	1·4068	56·4
1·3739	74·0	1·3845	68·1	1·3955	62·2	1·4070	56·3
1·3741	73·9	1·3847	68·0	1·3957	62·1	1·4071	56·2
1·3742	73·8	1·3849	67·9	1·3959	62·0	1·4073	56·1
1·3744	73·7	1·3850	67·8	1·3961	61·9	1·4075	56·0
1·3746	73·6	1·3852	67·7	1·3963	61·8	1·4077	55·9
1·3748	73·5	1·3854	67·6	1·3965	61·7	1·4079	55·8
1·3749	73·4	1·3856	67·5	1·3967	61·6	1·4081	55·7
1·3751	73·3	1·3858	67·4	1·3969	61·5	1·4083	55·6
1·3753	73·2	1·3860	67·3	1·3970	61·4	1·4085	55·5
1·3755	73·1	1·3862	67·2	1·3972	61·3	1·4087	55·4
1·3757	73·0	1·3863	67·1	1·3974	61·2	1·4089	55·3
1·3758	72·9	1·3865	67·0	1·3976	61·1	1·4091	55·2
1·3760	72·8	1·3867	66·9	1·3978	61·0	1·4093	55·1
1·3762	72·7	1·3869	66·8	1·3980	60·9	1·4095	55·0
1·3764	72·6	1·3871	66·7	1·3982	60·8	1·4097	54·9
1·3766	72·5	1·3873	66·6	1·3984	60·7	1·4099	54·8
1·3767	72·4	1·3874	66·5	1·3986	60·6	1·4101	54·7
1·3769	72·3	1·3876	66·4	1·3988	60·5	1·4103	54·6
1·3771	72·2	1·3878	66·3	1·3989	60·4	1·4106	54·5

TABLE XXVI—*continued.*

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1·4108	54·4	1·4232	48·5	1·4359	42·6	1·4496	36·7
1·4110	54·3	1·4234	48·4	1·4362	42·5	1·4498	36·6
1·4112	54·2	1·4236	48·3	1·4364	42·4	1·4500	36·5
1·4114	54·1	1·4238	48·2	1·4366	42·3	1·4503	36·4
1·4116	54·0	1·4240	48·1	1·4368	42·2	1·4505	36·3
1·4118	53·9	1·4242	48·0	1·4371	42·1	1·4507	36·2
1·4120	53·8	1·4244	47·9	1·4373	42·0	1·4509	36·1
1·4123	53·7	1·4246	47·8	1·4375	41·9	1·4512	36·0
1·4125	53·6	1·4248	47·7	1·4378	41·8	1·4514	35·9
1·4127	53·5	1·4250	47·6	1·4380	41·7	1·4516	35·8
1·4129	53·4	1·4253	47·5	1·4382	41·6	1·4519	35·7
1·4131	53·3	1·4255	47·4	1·4385	41·5	1·4521	35·6
1·4133	53·2	1·4257	47·3	1·4387	41·4	1·4523	35·5
1·4135	53·1	1·4259	47·2	1·4389	41·3	1·4526	35·4
1·4137	53·0	1·4261	47·1	1·4391	41·2	1·4528	35·3
1·4140	52·9	1·4263	47·0	1·4394	41·1	1·4530	35·2
1·4142	52·8	1·4265	46·9	1·4396	41·0	1·4533	35·1
1·4144	52·7	1·4267	46·8	1·4398	40·9	1·4535	35·0
1·4146	52·6	1·4269	46·7	1·4401	40·8	1·4537	34·9
1·4148	52·5	1·4271	46·6	1·4403	40·7	1·4540	34·8
1·4150	52·4	1·4273	46·5	1·4405	40·6	1·4542	34·7
1·4152	52·3	1·4275	46·4	1·4408	40·5	1·4544	34·6
1·4154	52·2	1·4277	46·3	1·4410	40·4	1·4547	34·5
1·4156	52·1	1·4279	46·2	1·4412	40·3	1·4549	34·4
1·4159	52·0	1·4281	46·1	1·4414	40·2	1·4551	34·3
1·4161	51·9	1·4283	46·0	1·4417	40·1	1·4554	34·2
1·4163	51·8	1·4285	45·9	1·4419	40·0	1·4556	34·1
1·4165	51·7	1·4288	45·8	1·4421	39·9	1·4558	34·0
1·4167	51·6	1·4290	45·7	1·4424	39·8	1·4561	33·9
1·4169	51·5	1·4292	45·6	1·4426	39·7	1·4563	33·8
1·4171	51·4	1·4294	45·5	1·4428	39·6	1·4565	33·7
1·4173	51·3	1·4296	45·4	1·4431	39·5	1·4567	33·6
1·4176	51·2	1·4298	45·3	1·4433	39·4	1·4570	33·5
1·4178	51·1	1·4300	45·2	1·4435	39·3	1·4572	33·4
1·4180	51·0	1·4302	45·1	1·4438	39·2	1·4574	33·3
1·4182	50·9	1·4304	45·0	1·4440	39·1	1·4577	33·2
1·4184	50·8	1·4306	44·9	1·4442	39·0	1·4579	33·1
1·4186	50·7	1·4309	44·8	1·4445	38·9	1·4581	33·0
1·4188	50·6	1·4311	44·7	1·4447	38·8	1·4584	32·9
1·4190	50·5	1·4313	44·6	1·4449	38·7	1·4586	32·8
1·4193	50·4	1·4316	44·5	1·4451	38·6	1·4588	32·7
1·4195	50·3	1·4318	44·4	1·4454	38·5	1·4591	32·6
1·4197	50·2	1·4320	44·3	1·4456	38·4	1·4593	32·5
1·4199	50·1	1·4322	44·2	1·4458	38·3	1·4595	32·4
1·4201	50·0	1·4325	44·1	1·4461	38·2	1·4598	32·3
1·4203	49·9	1·4327	44·0	1·4463	38·1	1·4600	32·2
1·4205	49·8	1·4329	43·9	1·4465	38·0	1·4602	32·1
1·4207	49·7	1·4332	43·8	1·4468	37·9	1·4605	32·0
1·4209	49·6	1·4334	43·7	1·4470	37·8	1·4607	31·9
1·4211	49·5	1·4336	43·6	1·4472	37·7	1·4609	31·8
1·4213	49·4	1·4339	43·5	1·4475	37·6	1·4612	31·7
1·4215	49·3	1·4341	43·4	1·4477	37·5	1·4614	31·6
1·4217	49·2	1·4343	43·3	1·4479	37·4	1·4616	31·5
1·4220	49·1	1·4345	43·2	1·4482	37·3	1·4619	31·4
1·4222	49·0	1·4348	43·1	1·4484	37·2	1·4621	31·3
1·4224	48·9	1·4350	43·0	1·4486	37·1	1·4623	31·2
1·4226	48·8	1·4352	42·9	1·4489	37·0	1·4625	31·1
1·4228	48·7	1·4355	42·8	1·4491	36·9	1·4628	31·0
1·4230	48·6	1·4357	42·7	1·4493	36·8	1·4630	30·9

TABLE XXVI—*continued.*

Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.	Refractive index at 20° C.	Per cent. water.
1.4632	30.8	1.4730	26.8	1.4830	22.8	1.4933	18.8
1.4635	30.7	1.4732	26.7	1.4832	22.7	1.4935	18.7
1.4637	30.6	1.4735	26.6	1.4835	22.6	1.4938	18.6
1.4639	30.5	1.4737	26.5	1.4838	22.5	1.4941	18.5
1.4642	30.4	1.4740	26.4	1.4840	22.4	1.4943	18.4
1.4644	30.3	1.4742	26.3	1.4843	22.3	1.4946	18.3
1.4646	30.2	1.4744	26.2	1.4845	22.2	1.4949	18.2
1.4649	30.1	1.4747	26.1	1.4848	22.1	1.4951	18.1
1.4651	30.0	1.4749	26.0	1.4850	22.0	1.4954	18.0
1.4653	29.9	1.4752	25.9	1.4853	21.9	1.4956	17.9
1.4656	29.8	1.4754	25.8	1.4855	21.8	1.4959	17.8
1.4658	29.7	1.4757	25.7	1.4858	21.7	1.4962	17.7
1.4661	29.6	1.4759	25.6	1.4860	21.6	1.4964	17.6
1.4663	29.5	1.4762	25.5	1.4863	21.5	1.4967	17.5
1.4666	29.4	1.4764	25.4	1.4865	21.4	1.4970	17.4
1.4668	29.3	1.4767	25.3	1.4868	21.3	1.4972	17.3
1.4671	29.2	1.4769	25.2	1.4871	21.2	1.4975	17.2
1.4673	29.1	1.4772	25.1	1.4873	21.1	1.4978	17.1
1.4676	29.0	1.4774	25.0	1.4876	21.0	1.4980	17.0
1.4678	28.9	1.4777	24.9	1.4878	20.9	1.4983	16.9
1.4681	28.8	1.4779	24.8	1.4881	20.8	1.4985	16.8
1.4683	28.7	1.4782	24.7	1.4883	20.7	1.4988	16.7
1.4685	28.6	1.4784	24.6	1.4886	20.6	1.4991	16.6
1.4688	28.5	1.4787	24.5	1.4888	20.5	1.4993	16.5
1.4690	28.4	1.4789	24.4	1.4891	20.4	1.4996	16.4
1.4693	28.3	1.4792	24.3	1.4893	20.3	1.4999	16.3
1.4695	28.2	1.4794	24.2	1.4896	20.2	1.5001	16.2
1.4698	28.1	1.4797	24.1	1.4898	20.1	1.5004	16.1
1.4700	28.0	1.4799	24.0	1.4901	20.0	1.5007	16.0
1.4703	27.9	1.4802	23.9	1.4904	19.9	1.5009	15.9
1.4705	27.8	1.4804	23.8	1.4906	19.8	1.5012	15.8
1.4708	27.7	1.4807	23.7	1.4909	19.7	1.5015	15.7
1.4710	27.6	1.4810	23.6	1.4912	19.6	1.5017	15.6
1.4713	27.5	1.4812	23.5	1.4914	19.5	1.5020	15.5
1.4715	27.4	1.4815	23.4	1.4917	19.4	1.5022	15.4
1.4717	27.3	1.4817	23.3	1.4919	19.3	1.5025	15.3
1.4720	27.2	1.4820	23.2	1.4922	19.2	1.5028	15.2
1.4722	27.1	1.4822	23.1	1.4925	19.1	1.5030	15.1
1.4725	27.0	1.4825	23.0	1.4927	19.0	1.5033	15.0
1.4727	26.9	1.4827	22.9	1.4930	18.9		

TABLE XXVII. (*Text*, p. 606.)

Table of Corrections for the Percentages of Water found below and above 20°, by means of the Abbé Refractometer. (Stanek.)

Temperature °C.	Percentage of water.									
	95.	90.	85.	80.	70.	60.	50.	40.	30.	25.
Add to the percentage of water.										
15	0·25	0·27	0·31	0·31	0·34	0·35	0·36	0·37	0·36	0·36
16	0·21	0·23	0·26	0·27	0·29	0·31	0·31	0·32	0·31	0·29
17	0·16	0·18	0·20	0·20	0·22	0·23	0·23	0·23	0·20	0·17
18	0·11	0·12	0·14	0·14	0·15	0·16	0·16	0·15	0·12	0·09
19	0·06	0·07	0·08	0·08	0·08	0·09	0·09	0·08	0·07	0·05
Subtract from the percentage of water.										
21	0·06	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07	0·07
22	0·12	0·14	0·14	0·14	0·14	0·14	0·15	0·14	0·14	0·14
23	0·18	0·20	0·20	0·21	0·21	0·21	0·23	0·21	0·22	0·22
24	0·24	0·26	0·26	0·27	0·28	0·28	0·30	0·28	0·29	0·29
25	0·30	0·32	0·32	0·34	0·36	0·36	0·38	0·36	0·36	0·37
26	0·36	0·39	0·39	0·41	0·43	0·43	0·46	0·44	0·43	0·44
27	0·43	0·46	0·46	0·48	0·50	0·51	0·55	0·62	0·50	0·51
28	0·50	0·53	0·53	0·55	0·58	0·59	0·63	0·70	0·57	0·59
29	0·57	0·60	0·61	0·62	0·66	0·67	0·71	0·78	0·65	0·67
30	0·64	0·67	0·70	0·71	0·74	0·75	0·80	0·86	0·73	0·75

TABLE XXVIII. (*Text*, p. 654.)

A Table for the Determination of the quantity of Juice and the Factors to be employed in the Estimation of the Reducing Sugar in Cane Juices. (Winter.)

Note.—H grams of juice are to be diluted to 200 c.c. after addition of basic lead acetate solution; 150 c.c. of the filtrate are treated with sodium sulphate, made up to 200 c.c. and filtered, 50 c.c. of the filtrate being boiled with 50 c.c. of Fehling's solution for two minutes. P = Rotation of the original juice; F = Factor; $F \times G'$ (see Table 54) = Percentage of Invert Sugar.

H.	P.	F.	H.	P.	F.	H.	P.	F.
80.00	10.0	6.67	57.14	14.0	9.33	44.44	18.0	12.00
79.21	1	73	56.74	1	40	44.20	1	07
78.43	2	80	56.34	2	47	43.96	2	13
77.67	3	87	55.94	3	53	43.72	3	20
76.92	4	93	55.55	4	60	43.48	4	27
76.19	5	7.00	55.17	5	67	43.24	5	33
75.47	6	07	54.79	6	73	43.01	6	40
74.77	7	13	54.42	7	80	42.78	7	47
74.07	8	20	54.05	8	87	42.55	8	53
73.39	9	27	53.69	9	93	42.33	9	60
72.72	11.0	7.33	53.33	15.0	10.00	42.11	19.0	12.67
72.07	1	40	52.98	1	07	41.89	1	73
71.43	2	47	52.63	2	13	41.67	2	80
70.80	3	53	52.29	3	20	41.45	3	87
70.18	4	60	51.95	4	27	41.24	4	93
69.57	5	67	51.61	5	33	41.03	5	13.00
68.97	6	73	51.28	6	40	40.82	6	07
68.38	7	80	50.95	7	47	40.61	7	13
67.80	8	87	50.63	8	53	40.40	8	20
67.23	9	93	50.31	9	60	40.20	9	27
66.67	12.0	8.00	50.00	16.0	10.67	40.00	20.0	13.33
66.12	1	07	49.69	1	73	39.80	1	40
65.57	2	13	49.38	2	80	39.60	2	47
65.04	3	20	49.08	3	87	39.41	3	53
64.52	4	27	48.78	4	93	39.22	4	60
64.00	5	33	48.48	5	11.00	39.02	5	67
63.49	6	40	48.19	6	07	38.83	6	73
62.99	7	47	47.90	7	13	38.64	7	80
62.50	8	53	47.62	8	20	38.46	8	87
62.02	9	60	47.34	9	27	38.28	9	93
61.54	13.0	8.67	47.06	17.0	11.33	38.10	21.0	14.00
61.07	1	73	46.78	1	40	37.92	1	07
60.61	2	80	46.51	2	46	37.74	2	13
60.15	3	87	46.24	3	53	37.56	3	20
59.70	4	93	45.97	4	60	37.38	4	27
59.26	5	9.00	45.71	5	67	37.21	5	33
58.82	6	07	45.45	6	73	37.04	6	40
58.39	7	13	45.20	7	80	36.87	7	47
57.97	8	20	44.94	8	87	36.70	8	53
57.55	9	27	44.69	9	93	36.53	9	60

TABLE XXIX. (*Text, pp. 655-56.*)

A Table for the Determination of Invert Sugar (G') from the quantity of Sodium Hydroxide equivalent to the Cuprous Oxide obtained in the Estimation of the Reducing Sugar in Cane Juices. (Winter.)

[*Note* : In order to determine the percentage of invert sugar in a juice, the cuprous oxide is dissolved in 20 c.c. of standard hydrochloric acid, the amount of sodium hydroxide equivalent to the cuprous oxide being found by titration of the excess of acid. In the following Table G' corresponds to the quantity of invert sugar contained in 50 c.c. of the diluted solution. The percentage of invert sugar in the original juice is found by multiplying G' by the factor F (see Table 53), which corresponds to the rotation of the juice. From the column headed "Cu" the percentage of invert sugar may be calculated when the gravimetric method is used.]

Cu.	G'.	NaOH.	Cu.	G'.	NaOH.	Cu.	G'.	NaOH.
...	0.070	0.0269	0.0885	0.110	0.0473	0.1391
...	71	0274	0898	111	0478	1404
...	72	0279	0911	112	0483	1417
...	73	0284	0923	113	0488	1429
...	74	0289	0936	114	0493	1442
0.035	0.0092	0.0443	75	0294	0949	115	0499	1455
36	0097	0455	76	0299	0961	116	0504	1467
37	0102	0468	77	0304	0974	117	0509	1480
38	0107	0481	78	0309	0987	118	0514	1493
39	0112	0493	79	0314	0999	119	0520	1505
0.040	0.0117	0.0506	0.080	0.0319	0.1012	0.120	0.0526	0.1518
41	0122	0519	81	0324	1025	121	0531	1531
42	0127	0531	82	0329	1037	122	0536	1543
43	0132	0544	83	0334	1050	123	0542	1556
44	0137	0557	84	0339	1063	124	0548	1569
45	0142	0569	85	0344	1075	125	0554	1582
46	0147	0582	86	0349	1088	126	0559	1594
47	0152	0594	87	0354	1100	127	0564	1606
48	0157	0607	88	0359	1113	128	0570	1619
49	0162	0620	89	0364	1126	129	0576	1632
0.050	0.0167	0.0632	0.090	0.0370	0.1138	0.130	0.0581	0.1644
51	0172	0645	91	0375	1151	131	0586	1657
52	0177	0658	92	0380	1164	132	0591	1670
53	0182	0670	93	0385	1176	133	0597	1682
54	0187	0683	94	0390	1189	134	0603	1695
55	0192	0696	95	0395	1202	135	0608	1708
56	0197	0708	96	0400	1214	136	0613	1720
57	0202	0721	97	0405	1227	137	0618	1733
58	0207	0734	98	0410	1240	138	0624	1746
59	0212	0746	99	0415	1252	139	0630	1758
0.060	0.0218	0.0759	0.100	0.0421	0.1265	0.140	0.0635	0.1771
61	0223	0772	101	0426	1278	141	0640	1783
62	0228	0784	102	0431	1290	142	0645	1796
63	0233	0797	103	0436	1303	143	0651	1809
64	0238	0810	104	0441	1316	144	0657	1821
65	0243	0822	105	0447	1328	145	0662	1834
66	0248	0835	106	0452	1341	146	0667	1847
67	0253	0847	107	0457	1353	147	0672	1859
68	0258	0860	108	0462	1366	148	0678	1872
69	0263	0873	109	0467	1379	149	0684	1885

TABLE XXIX—*continued.*

Cu.	G'.	NaOH.	Cu.	G'.	NaOH.	Cu.	G'.	NaOH.
0·150	0·0689	0·1897	0·200	0·0970	0·2530	0·250	0·1266	0·3162
151	0694	1910	201	0975	2542	251	1271	3175
152	0699	1923	202	0981	2555	252	1277	3188
153	0705	1935	203	0987	2568	253	1283	3200
154	0711	1948	204	0993	2580	254	1289	3213
155	0716	1961	205	0999	2593	255	1295	3226
156	0721	1973	206	1005	2606	256	1300	3238
157	0726	1986	207	1011	2618	257	1306	3251
158	0732	1999	208	1017	2631	258	1312	3264
159	0738	2011	209	1023	2644	259	1318	3276
0·160	0·0744	0·2024	0·210	0·1029	0·2656	0·260	0·1324	0·3289
161	0749	2036	211	1035	2669	261	1329	3301
162	0754	2049	212	1041	2682	262	1335	3314
163	0760	2062	213	1047	2694	263	1341	3327
164	0766	2074	214	1053	2707	264	1347	3339
165	0772	2087	215	1059	2920	265	1353	3352
166	0777	2100	216	1065	2732	266	1358	3365
167	0782	2112	217	1071	2745	267	1364	3377
168	0788	2125	218	1077	2758	268	1370	3390
169	0794	2138	219	1083	2770	269	1376	3403
0·170	0·0800	0·2150	0·220	0·1089	0·2783	0·270	0·1382	0·3415
171	0805	2163	221	1095	2795	271	1387	3428
172	0810	2176	222	1101	2808	272	1393	3441
173	0816	2188	223	1107	2821	273	1399	3453
174	0822	2201	224	1113	2833	274	1405	3466
175	0828	2214	225	1119	2846	275	1411	3479
176	0833	2226	226	1125	2859	276	1416	3491
177	0838	2239	227	1131	2871	277	1422	3504
178	0844	2252	228	1137	2884	278	1428	3516
179	0850	2264	229	1143	2897	279	1434	3529
0·180	0·0856	0·2277	0·230	0·1149	0·2909	0·280	0·1440	0·3542
181	0861	2289	231	1155	2922	281	1445	3554
182	0866	2302	232	1161	2935	282	1451	3567
183	0872	2315	233	1167	2947	283	1457	3580
184	0878	2327	234	1173	2960	284	1463	3592
185	0884	2340	235	1179	2973	285	1469	3605
186	0889	2353	236	1184	2985	286	1474	3618
187	0894	2365	237	1190	2998	287	1480	3630
188	0900	2378	238	1196	3011	288	1486	3643
189	0906	2391	239	1202	3023	289	1492	3656
0·190	0·0912	0·2403	0·240	0·1208	0·3036	0·290	0·1498	0·3668
191	0917	2416	241	1213	3048	291	1503	3681
192	0923	2429	242	1219	3061	292	1509	3694
193	0929	2441	243	1225	3074	293	1515	3706
194	0935	2454	244	1231	3086	294	1521	3719
195	0941	2467	245	1237	3099	295	1527	3732
196	0946	2479	246	1242	3112	296	1532	3744
197	0952	2492	247	1248	3124	297	1538	3757
198	0958	2505	248	1254	3137	298	1544	3769
199	0964	2517	249	1260	3150	299	1550	3782

TABLE XXX. (*Text, p. 676.*)

Table for Estimating the Content of Water in Starch.
(Scheibler.)

Water- content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.	Water- content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.	Water- content of starch flour.	Degrees Tralles.	Specific gravity of alcohol.
Per cent.			Per cent.			Per cent.		
0	93.3	0.8226	22	86.4	0.8455	44	79.7	0.8643
1	93.1	0.8234	23	86.1	0.8465	45	79.5	0.8651
2	92.9	0.8243	24	85.8	0.8474	46	79.2	0.8658
3	92.6	0.8253	25	85.5	0.8484	47	78.9	0.8665
4	92.3	0.8262	26	85.2	0.8493	48	78.6	0.8673
5	92.0	0.8271	27	84.9	0.8502	49	78.4	0.8680
6	91.7	0.8281	28	84.6	0.8511	50	78.1	0.8688
7	91.4	0.8291	29	84.3	0.8520	51	77.8	0.8695
8	91.2	0.8300	30	84.0	0.8529	52	77.5	0.8703
9	90.9	0.8311	31	83.7	0.8538	53	77.3	0.8710
10	90.5	0.8323	32	83.4	0.8547	54	77.1	0.8716
11	90.1	0.8335	33	83.1	0.8555	55	76.8	0.8723
12	89.8	0.8346	34	82.8	0.8563	56	76.5	0.8731
13	89.5	0.8358	35	82.5	0.8571	57	76.3	0.8738
14	89.1	0.8370	36	82.2	0.8579	58	76.0	0.8745
15	88.7	0.8382	37	81.9	0.8587	59	75.7	0.8753
16	88.3	0.8394	38	81.6	0.8595	60	75.4	0.8760
17	88.0	0.8405	39	81.3	0.8603	61	75.2	0.8767
18	87.7	0.8416	40	80.9	0.8612	62	74.9	0.8775
19	87.4	0.8426	41	80.6	0.8620	63	74.6	0.8783
20	87.1	0.8436	42	80.3	0.8627	64	74.3	0.8791
21	86.7	0.8446	43	80.0	0.8635	65	74.0	0.8798

TABLE XXXI. (*Text, p. 677.*)

Table for Estimating the content of Water in Starch from its Specific Gravity. (Saare.)

Weight obtained.	Water- content of the starch.	Weight obtained.	Water- content of the starch.	Weight obtained.	Water- content of the starch.	Weight obtained.	Water- content of the starch.
g.	Per cent.	g.	Per cent.	g.	Per cent.	g.	Per cent.
289.40	0	288.10	16	277.20	31	271.25	46
289.00	1	282.70	17	276.80	32	270.90	47
288.60	2	282.30	18	276.40	33	270.50	48
288.20	3	281.90	19	276.00	34	270.10	49
287.80	4	281.50	20	275.60	35	269.70	50
287.40	5	281.10	21	275.20	36	269.30	51
287.05	6	280.75	22	274.80	37	268.90	52
286.65	7	280.35	23	274.40	38	268.50	53
286.25	8	279.95	24	274.05	39	268.10	54
285.85	9	279.55	25	273.65	40	267.75	55
285.45	10	279.15	26	273.25	41	267.35	56
285.05	11	278.75	27	272.85	42	266.95	57
284.65	12	278.35	28	272.45	43	266.55	58
284.25	13	277.95	29	272.05	44	266.15	59
283.90	14	277.60	30	271.65	45	265.75	60
283.50	15						

TABLE XXXII. (*Text, pp. 711-12.*)

Table of Specific Gravities of Mixtures of Alcohol and Water.
(T. Stevenson.)

Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.	Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.
0.7938	100.00	100.00	175.25	0.8440	81.65	86.80	152.1
0.7940	99.95	99.95	175.2	0.8450	81.20	86.50	151.5
0.7950	99.60	99.75	174.8	0.8460	80.80	86.15	150.9
0.7960	99.30	99.55	174.4	0.8470	80.45	85.90	150.3
0.7970	98.95	99.40	174.1	0.8480	80.05	85.50	149.7
0.7980	98.65	99.20	173.8	0.8490	79.60	85.15	149.1
0.7990	98.35	99.00	173.5	0.8500	79.20	84.80	148.6
0.8000	98.00	98.75	173.1	0.8510	78.80	84.45	148.0
0.8010	97.70	98.55	172.7	0.8520	78.40	84.15	147.4
0.8020	97.35	98.40	172.4	0.8530	78.00	83.80	146.7
0.8030	97.05	98.15	172.0	0.8540	77.55	83.45	146.2
0.8040	96.70	97.95	171.6	0.8550	77.15	83.15	145.6
0.8050	96.35	97.70	171.2	0.8560	76.70	82.75	145.0
0.8060	96.05	97.50	170.8	0.8570	76.30	82.40	144.4
0.8070	95.70	97.25	170.4	0.8580	75.85	82.00	143.8
0.8080	95.30	97.05	170.0	0.8590	75.50	81.70	143.2
0.8090	94.95	96.80	169.6	0.8600	75.10	81.35	142.6
0.8100	94.60	96.55	169.2	0.8610	74.70	81.00	141.9
0.8110	94.30	96.35	168.8	0.8620	74.25	80.60	141.3
0.8120	93.95	96.10	168.4	0.8630	73.80	80.25	140.7
0.8130	93.55	95.80	167.9	0.8640	73.45	79.95	140.1
0.8140	93.20	95.50	167.4	0.8650	73.00	79.55	139.4
0.8150	92.80	95.25	167.0	0.8660	72.55	79.15	138.8
0.8160	92.45	95.00	166.5	0.8670	72.20	78.75	138.1
0.8170	92.05	94.75	166.1	0.8680	71.75	78.45	137.4
0.8180	91.70	94.50	165.6	0.8690	71.30	78.10	136.6
0.8190	91.35	94.25	165.1	0.8700	70.85	77.70	136.1
0.8200	90.95	94.00	164.7	0.8710	70.50	77.35	135.6
0.8210	90.65	93.75	164.3	0.8720	70.05	76.95	134.9
0.8220	90.25	93.50	163.9	0.8730	69.65	76.60	134.3
0.8230	89.90	93.25	163.4	0.8740	69.20	76.15	133.5
0.8240	89.50	92.90	162.8	0.8750	68.80	75.80	132.9
0.8250	89.05	92.55	162.2	0.8760	68.40	75.45	132.2
0.8260	88.65	92.30	161.7	0.8770	67.95	75.10	131.6
0.8270	88.30	92.00	161.2	0.8780	67.55	74.70	130.9
0.8280	87.90	91.70	160.7	0.8790	67.05	74.30	130.2
0.8290	87.50	91.40	160.2	0.8800	66.65	73.90	129.6
0.8300	87.15	91.10	159.7	0.8810	66.25	73.50	128.9
0.8310	86.75	90.85	159.1	0.8820	65.80	73.15	128.2
0.8320	86.35	90.55	158.6	0.8830	65.40	72.75	127.5
0.8330	85.95	90.25	158.1	0.8840	65.00	72.35	126.8
0.8340	85.60	89.95	157.6	0.8850	64.55	71.90	126.0
0.8350	85.20	89.60	157.1	0.8860	64.15	71.60	125.4
0.8360	84.80	89.30	156.5	0.8870	63.70	71.20	124.7
0.8370	84.40	89.00	156.0	0.8880	63.25	70.75	124.0
0.8380	84.00	88.65	155.4	0.8890	62.85	70.35	123.3
0.8390	83.60	88.35	154.9	0.8900	62.45	69.95	122.6
0.8400	83.20	88.05	154.3	0.8910	62.00	69.60	121.9
0.8410	82.80	87.75	153.8	0.8920	61.55	69.15	121.1
0.8420	82.45	87.45	153.2	0.8930	61.10	68.75	120.5
0.8430	82.00	87.10	152.7	0.8940	60.70	68.35	119.8

TABLE XXXII—*continued.*

Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.	Specific gravity at 60° F.	Percentage of alcohol by weight.	Percentage of alcohol by volume.	Percentage of proof spirit.
0.8950	60.30	68.00	119.2	0.9480	35.50	42.40	74.3
0.8960	59.85	67.55	118.4	0.9490	35.00	41.85	73.3
0.8970	59.35	67.05	117.5	0.9500	34.40	41.20	72.2
0.8980	58.95	66.65	116.8	0.9510	33.85	40.55	71.0
0.8990	58.55	66.30	116.2	0.9520	33.30	39.90	70.0
0.9000	58.05	65.80	115.4	0.9530	32.70	39.20	68.7
0.9010	57.60	65.35	114.6	0.9540	32.15	38.60	67.6
0.9020	57.20	65.00	113.9	0.9550	31.55	37.95	66.5
0.9030	56.75	64.55	113.1	0.9560	31.00	37.35	65.4
0.9040	56.35	64.10	112.3	0.9570	30.35	36.55	64.1
0.9050	55.90	63.70	111.6	0.9580	29.70	35.85	62.8
0.9060	55.45	63.30	110.9	0.9590	29.10	35.10	61.6
0.9070	54.95	62.80	110.0	0.9600	28.45	34.40	60.3
0.9080	54.55	62.60	109.3	0.9610	27.80	33.60	59.0
0.9090	54.10	61.95	108.5	0.9620	27.15	32.90	57.6
0.9100	53.65	61.50	107.8	0.9630	26.45	32.05	56.2
0.9110	53.25	61.05	107.0	0.9640	25.70	31.20	54.7
0.9120	52.80	60.65	106.3	0.9650	25.00	30.40	53.3
0.9130	52.35	60.15	105.5	0.9660	24.25	29.55	51.8
0.9140	51.90	59.75	104.7	0.9670	23.50	28.65	50.2
0.9150	51.45	59.30	103.9	0.9680	22.75	27.75	48.6
0.9160	51.00	58.85	103.1	0.9690	21.95	26.85	46.9
0.9170	50.55	58.40	102.3	0.9700	21.10	25.75	45.2
0.9180	50.10	57.90	101.5	0.9710	20.35	24.90	43.6
0.9190	49.65	57.40	100.6	0.9720	19.55	23.90	42.0
0.9198	49.25	57.05	100.0	0.9730	18.80	23.05	40.5
0.9200	49.15	56.95	99.8	0.9740	17.90	21.95	38.5
0.9210	48.65	56.50	99.0	0.9750	17.10	21.00	36.8
0.9220	48.25	56.05	98.2	0.9760	16.30	20.00	35.1
0.9230	47.80	55.55	97.4	0.9770	15.45	19.00	33.3
0.9240	47.30	55.10	96.5	0.9780	14.65	18.00	31.6
0.9250	46.90	54.60	95.6	0.9790	13.80	17.00	29.8
0.9260	46.40	54.10	94.8	0.9800	13.00	16.00	28.0
0.9270	45.95	53.65	94.1	0.9810	12.25	15.10	26.5
0.9280	45.50	53.15	93.2	0.9820	11.45	14.10	24.7
0.9290	45.00	52.70	92.3	0.9830	10.65	13.20	23.1
0.9300	44.55	52.15	91.4	0.9840	9.90	12.35	21.5
0.9310	44.10	51.70	90.6	0.9850	9.20	11.40	20.0
0.9320	43.60	51.20	89.8	0.9860	8.50	10.55	18.4
0.9330	43.15	50.70	88.9	0.9870	7.80	9.65	16.9
0.9340	42.60	50.15	87.9	0.9880	7.10	8.80	15.5
0.9350	42.15	49.65	87.0	0.9890	6.40	8.00	14.1
0.9360	41.65	49.10	86.1	0.9900	5.75	7.15	12.6
0.9370	41.15	48.60	85.1	0.9910	5.15	6.40	11.2
0.9380	40.65	48.05	84.1	0.9920	4.50	5.65	9.9
0.9390	40.15	47.50	83.3	0.9930	3.90	4.90	8.6
0.9400	39.70	47.00	82.4	0.9940	3.30	4.15	7.2
0.9410	39.15	46.40	81.4	0.9950	2.75	3.50	6.1
0.9420	38.65	45.85	80.4	0.9960	2.15	2.70	4.9
0.9430	38.20	45.40	79.5	0.9970	1.60	2.00	3.5
0.9440	37.65	44.75	78.4	0.9980	1.05	1.30	2.4
0.9450	37.10	44.15	77.6	0.9990	0.55	0.65	1.2
0.9460	36.55	43.60	76.4	0.9999	0.05	0.05	0.1
0.9470	36.05	43.00	75.4				

TABLE XXXIII. (*Text*, p. 729.)

The Estimation of Higher Alcohols in Potable Spirits.

Table for Distillates containing less than 24.7 per cent. of Alcohol by Weight.

Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of absolute alcohol to be added to 100 c.c. of distillate.
22.50	3.52	23.05	2.63	23.60	1.74	24.15	0.85
22.55	3.44	23.10	2.55	23.65	1.66	24.20	0.77
22.60	3.36	23.15	2.47	23.70	1.58	24.25	0.69
22.65	3.28	23.20	2.39	23.75	1.50	24.30	0.61
22.70	3.20	23.25	2.31	23.80	1.42	24.35	0.53
22.75	3.11	23.30	2.23	23.85	1.34	24.40	0.45
22.80	3.04	23.35	2.15	23.90	1.26	24.45	0.37
22.85	2.96	23.40	2.07	23.95	1.18	24.50	0.29
22.90	2.88	23.45	1.98	24.00	1.09	24.55	0.21
22.95	2.79	23.50	1.90	24.05	1.01	24.60	0.12
23.00	2.71	23.55	1.82	24.10	0.93	24.65	0.04

TABLE XXXIV. (*Text*, pp. 730-32.)

The Estimation of Higher Alcohols in Potable Spirits.

Table for Distillates containing more than 24.7 per cent. of Alcohol by Weight.

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
24.7	0.1	29.9	20.3	35.1	40.1	40.3	59.5	45.5	78.3	50.7	96.7
24.8	0.5	30.0	20.7	35.2	40.5	40.4	59.8	45.6	78.7	50.8	97.1
24.9	0.9	30.1	21.0	35.3	40.8	40.5	60.2	45.7	79.1	50.9	97.4
25.0	1.3	30.2	21.4	35.4	41.2	40.6	60.6	45.8	79.4	51.0	97.8
25.1	1.7	30.3	21.8	35.5	41.6	40.7	60.9	45.9	79.8	51.1	98.1
25.2	2.0	30.4	22.2	35.6	42.0	40.8	61.3	46.0	80.1	51.2	98.5
25.3	2.4	30.5	22.6	35.7	42.3	40.9	61.7	46.1	80.5	51.3	98.8
25.4	2.8	30.6	23.0	35.8	42.7	41.0	62.0	46.2	80.8	51.4	99.1
25.5	3.2	30.7	23.3	35.9	43.1	41.1	62.4	46.3	81.2	51.5	99.5
25.6	3.6	30.8	23.7	36.0	43.5	41.2	62.8	46.4	81.6	51.6	99.8
25.7	4.0	30.9	24.1	36.1	43.8	41.3	63.1	46.5	81.9	51.7	100.2
25.8	4.4	31.0	24.5	36.2	44.2	41.4	63.5	46.6	82.3	51.8	100.5
25.9	4.8	31.1	24.9	36.3	44.6	41.5	63.9	46.7	82.6	51.9	100.9
26.0	5.2	31.2	25.3	36.4	45.0	41.6	64.2	46.8	83.0	52.0	101.2
26.1	5.6	31.3	25.6	36.5	45.3	41.7	64.6	46.9	83.3	52.1	101.6
26.2	5.9	31.4	26.0	36.6	45.7	41.8	65.0	47.0	83.7	52.2	101.9
26.3	6.3	31.5	26.4	36.7	46.1	41.9	65.3	47.1	84.1	52.3	102.3
26.4	6.7	31.6	26.8	36.8	46.5	42.0	65.7	47.2	84.4	52.4	102.6
26.5	7.1	31.7	27.2	36.9	46.8	42.1	66.1	47.3	84.8	52.5	102.9
26.6	7.5	31.8	27.6	37.0	47.2	42.2	66.4	47.4	85.1	52.6	103.3
26.7	7.9	31.9	27.9	37.1	47.6	42.3	66.8	47.5	85.5	52.7	103.6
26.8	8.3	32.0	28.3	37.2	48.0	42.4	67.1	47.6	85.8	52.8	104.0
26.9	8.7	32.1	28.7	37.3	48.3	42.5	67.5	47.7	86.2	52.9	104.3
27.0	9.1	32.2	29.1	37.4	48.7	42.6	67.9	47.8	86.5	53.0	104.7
27.1	9.4	32.3	29.5	37.5	49.1	42.7	68.2	47.9	86.9	53.1	105.0
27.2	9.8	32.4	29.8	37.6	49.5	42.8	68.6	48.0	87.2	53.2	105.3
27.3	10.2	32.5	30.2	37.7	49.8	42.9	69.0	48.1	87.6	53.3	105.7
27.4	10.6	32.6	30.6	37.8	50.2	43.0	69.3	48.2	87.9	53.4	106.0
27.5	11.0	32.7	31.0	37.9	50.6	43.1	69.7	48.3	88.3	53.5	106.4
27.6	11.4	32.8	31.4	38.0	51.0	43.2	70.0	48.4	88.7	53.6	106.7
27.7	11.8	32.9	31.7	38.1	51.4	43.3	70.4	48.5	89.0	53.7	107.1
27.8	12.2	33.0	32.1	38.2	51.7	43.4	70.8	48.6	89.4	53.8	107.4
27.9	12.6	33.1	32.5	38.3	52.1	43.5	71.1	48.7	89.7	53.9	107.7
28.0	12.9	33.2	32.9	38.4	52.4	43.6	71.5	48.8	90.1	54.0	108.1
28.1	13.3	33.3	33.3	38.5	52.8	43.7	71.9	48.9	90.4	54.1	108.4
28.2	13.7	33.4	33.7	38.6	53.2	43.8	72.3	49.0	90.8	54.2	108.8
28.3	14.1	33.5	34.0	38.7	53.5	43.9	72.6	49.1	91.1	54.3	109.1
28.4	14.5	33.6	34.4	38.8	53.9	44.0	72.9	49.2	91.5	54.4	109.5
28.5	14.9	33.7	34.8	38.9	54.3	44.1	73.3	49.3	91.8	54.5	109.8
28.6	15.3	33.8	35.2	39.0	54.7	44.2	73.7	49.4	92.2	54.6	110.1
28.7	15.6	33.9	35.5	39.1	55.0	44.3	74.0	49.5	92.5	54.7	110.5
28.8	16.0	34.0	35.9	39.2	55.4	44.4	74.4	49.6	92.9	54.8	110.8
28.9	16.4	34.1	36.3	39.3	55.7	44.5	74.7	49.7	93.2	54.9	111.2
29.0	16.8	34.2	36.7	39.4	56.1	44.6	75.1	49.8	93.6	55.0	111.5
29.1	17.2	34.3	37.1	39.5	56.5	44.7	75.5	49.9	93.9	55.1	111.8
29.2	17.6	34.4	37.4	39.6	56.9	44.8	75.8	50.0	94.3	55.2	112.2
29.3	18.0	34.5	37.8	39.7	57.2	44.9	76.2	50.1	94.6	55.3	112.5
29.4	18.3	34.6	38.2	39.8	57.6	45.0	76.5	50.2	95.0	55.4	112.9
29.5	18.7	34.7	38.6	39.9	58.0	45.1	76.9	50.3	95.3	55.5	113.2
29.6	19.1	34.8	39.0	40.0	58.4	45.2	77.3	50.4	95.7	55.6	113.5
29.7	19.5	34.9	39.3	40.1	58.7	45.3	77.6	50.5	96.0	55.7	113.9
29.8	19.9	35.0	39.7	40.2	59.1	45.4	78.0	50.6	96.4	55.8	114.2

TABLE XXXIV—*continued.*

Table for Distillates

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
55.9	114.6	61.2	132.2	66.5	149.3	71.8	165.8	77.1	181.8	82.4	197.1
56.0	114.9	61.3	132.5	66.6	149.6	71.9	166.1	77.2	182.1	82.5	197.4
56.1	115.2	61.4	132.9	66.7	149.9	72.0	166.4	77.3	182.4	82.6	197.7
56.2	115.6	61.5	133.2	66.8	150.2	72.1	166.7	77.4	182.6	82.7	197.9
56.3	115.9	61.6	133.5	66.9	150.6	72.2	167.0	77.5	182.9	82.8	198.2
56.4	116.2	61.7	133.8	67.0	150.9	72.3	167.4	77.6	183.2	82.9	198.5
56.5	116.6	61.8	134.2	67.1	151.2	72.4	167.7	77.7	183.5	83.0	198.8
56.6	116.9	61.9	134.5	67.2	151.5	72.5	168.0	77.8	183.8	83.1	199.1
56.7	117.3	62.0	134.8	67.3	151.8	72.6	168.3	77.9	184.1	83.2	199.4
56.8	117.6	62.1	135.2	67.4	152.1	72.7	168.6	78.0	184.4	83.3	199.6
56.9	117.9	62.2	135.5	67.5	152.5	72.8	168.9	78.1	184.7	83.4	199.9
57.0	118.3	62.3	135.8	67.6	152.8	72.9	169.2	78.2	185.0	83.5	200.2
57.1	118.6	62.4	136.1	67.7	153.1	73.0	169.5	78.3	185.3	83.6	200.5
57.2	118.9	62.5	136.5	67.8	153.4	73.1	169.8	78.4	185.6	83.7	200.8
57.3	119.3	62.6	136.8	67.9	153.7	73.2	170.1	78.5	185.9	83.8	201.0
57.4	119.6	62.7	137.1	68.0	154.0	73.3	170.4	78.6	186.2	83.9	201.3
57.5	119.9	62.8	137.4	68.1	154.4	73.4	170.7	78.7	186.5	84.0	201.6
57.6	120.3	62.9	137.8	68.2	154.7	73.5	171.0	78.8	186.7	84.1	201.9
57.7	120.6	63.0	138.1	68.3	155.0	73.6	171.3	78.9	187.0	84.2	202.1
57.8	120.9	63.1	138.4	68.4	155.3	73.7	171.6	79.0	187.3	84.3	202.4
57.9	121.3	63.2	138.7	68.5	155.6	73.8	171.9	79.1	187.6	84.4	202.7
58.0	121.6	63.3	139.0	68.6	155.9	73.9	172.2	79.2	187.9	84.5	203.0
58.1	122.0	63.4	139.4	68.7	156.2	74.0	172.5	79.3	188.2	84.6	203.3
58.2	122.3	63.5	139.7	68.8	156.5	74.1	172.8	79.4	188.5	84.7	203.5
58.3	122.6	63.6	140.0	68.9	156.9	74.2	173.1	79.5	188.8	84.8	203.8
58.4	123.0	63.7	140.3	69.0	157.2	74.3	173.4	79.6	189.1	84.9	204.1
58.5	123.3	63.8	140.7	69.1	157.5	74.4	173.7	79.7	189.4	85.0	204.4
58.6	123.6	63.9	141.0	69.2	157.8	74.5	174.0	79.8	189.6	85.1	204.6
58.7	124.0	64.0	141.3	69.3	158.1	74.6	174.3	79.9	189.9	85.2	204.9
58.8	124.3	64.1	141.6	69.4	158.4	74.7	174.6	80.0	190.2	85.3	205.2
58.9	124.6	64.2	142.0	69.5	158.7	74.8	174.9	80.1	190.5	85.4	205.5
59.0	124.9	64.3	142.3	69.6	159.0	74.9	175.2	80.2	190.8	85.5	205.7
59.1	125.3	64.4	142.6	69.7	159.3	75.0	175.5	80.3	191.1	85.6	206.0
59.2	125.6	64.5	142.9	69.8	159.7	75.1	175.8	80.4	191.4	85.7	206.3
59.3	125.9	64.6	143.2	69.9	160.0	75.2	176.1	80.5	191.7	85.8	206.6
59.4	126.3	64.7	143.6	70.0	160.3	75.3	176.4	80.6	192.0	85.9	206.8
59.5	126.6	64.8	143.9	70.1	160.6	75.4	176.7	80.7	192.2	86.0	207.1
59.6	126.9	64.9	144.2	70.2	160.9	75.5	177.0	80.8	192.5	86.1	207.4
59.7	127.3	65.0	144.5	70.3	161.2	75.6	177.3	80.9	192.8	86.2	207.7
59.8	127.6	65.1	144.8	70.4	161.5	75.7	177.6	81.0	193.1	86.3	207.9
59.9	127.9	65.2	145.2	70.5	161.8	75.8	177.9	81.1	193.4	86.4	208.2
60.0	128.3	65.3	145.5	70.6	162.1	75.9	178.2	81.2	193.7	86.5	208.5
60.1	128.6	65.4	145.8	70.7	162.4	76.0	178.5	81.3	194.0	86.6	208.8
60.2	128.9	65.5	146.1	70.8	162.8	76.1	178.8	81.4	194.3	86.7	209.0
60.3	129.2	65.6	146.4	70.9	163.1	76.2	179.1	81.5	194.5	86.8	209.3
60.4	129.6	65.7	146.8	71.0	163.4	76.3	179.4	81.6	194.8	86.9	209.6
60.5	129.9	65.8	147.1	71.1	163.7	76.4	179.7	81.7	195.1	87.0	209.9
60.6	130.2	65.9	147.4	71.2	164.0	76.5	180.0	81.8	195.4	87.1	210.1
60.7	130.6	66.0	147.7	71.3	164.3	76.6	180.3	81.9	195.7	87.2	210.4
60.8	130.9	66.1	148.0	71.4	164.6	76.7	180.6	82.0	196.0	87.3	210.7
60.9	131.2	66.2	148.3	71.5	164.9	76.8	180.9	82.1	196.2	87.4	210.9
61.0	131.5	66.3	148.7	71.6	165.2	76.9	181.2	82.2	196.5	87.5	211.2
61.1	131.9	66.4	149.0	71.7	165.5	77.0	181.5	82.3	196.8	87.6	211.5

TABLE XXXIV—*continued.*

Table for Distillates

Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.	Percentage of alcohol by weight in distillate.	c.c. of water to be added to 100 c.c. of distillate.
87.7	211.7	89.8	217.3	91.9	222.8	94.0	228.1	96.1	233.3	98.1	238.1
87.8	212.0	89.9	217.6	92.0	223.1	94.1	228.4	96.2	233.5	98.2	238.3
87.9	212.3	90.0	217.9	92.1	223.3	94.2	228.6	96.3	233.8	98.3	238.5
88.0	212.6	90.1	218.1	92.2	223.6	94.3	228.9	96.4	234.0	98.4	238.8
88.1	212.8	90.2	218.4	92.3	223.8	94.4	229.1	96.5	234.3	98.5	239.0
88.2	213.1	90.3	218.7	92.4	224.1	94.5	229.4	96.6	234.5	98.6	239.2
88.3	213.4	90.4	218.9	92.5	224.3	94.6	229.6	96.7	234.7	98.7	239.5
88.4	213.6	90.5	219.2	92.6	224.6	94.7	229.9	96.8	235.0	98.8	239.7
88.5	213.9	90.6	219.4	92.7	224.9	94.8	230.1	96.9	235.2	98.9	239.9
88.6	214.2	90.7	219.7	92.8	225.1	94.9	230.4	97.0	235.5	99.0	240.1
88.7	214.4	90.8	220.0	92.9	225.4	95.0	230.6	97.1	235.7	99.1	240.4
88.8	214.7	90.9	220.2	93.0	225.6	95.1	230.9	97.2	235.9	99.2	240.6
88.9	215.0	91.0	220.5	93.1	225.9	95.2	231.1	97.3	236.2	99.3	240.8
89.0	215.2	91.1	220.7	93.2	226.1	95.3	231.3	97.4	236.4	99.4	241.1
89.1	215.5	91.2	221.0	93.3	226.4	95.4	231.6	97.5	236.6	99.5	241.3
89.2	215.8	91.3	221.3	93.4	226.6	95.5	231.9	97.6	236.9	99.6	241.5
89.3	216.0	91.4	221.5	93.5	226.9	95.6	232.1	97.7	237.1	99.7	241.8
89.4	216.3	91.5	221.8	93.6	227.1	95.7	232.3	97.8	237.3	99.8	242.0
89.5	216.6	91.6	222.0	93.7	227.4	95.8	232.6	97.9	237.6	99.9	242.2
89.6	216.8	91.7	222.3	93.8	227.6	95.9	232.8	98.0	237.8	100.0	242.4
89.7	217.1	91.8	222.5	93.9	227.9	96.0	233.1				

TABLE XXXV. (*Text*, pp. 760-62.)

Table for the Determination of E, which governs the choice of Method to be used for the Estimation of the Extract in Wines. (K. Windisch.)

<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.
1·0000	0·00	1·0100	2·58	1·0200	5·17	1·0300	7·76	1·0400	10·35
2	0·05	2	2·63	2	5·22	2	7·81	2	10·40
4	0·10	4	2·69	4	5·27	4	7·86	4	10·45
6	0·15	6	2·74	6	5·32	6	7·91	6	10·51
8	0·20	8	2·79	8	5·38	8	7·97	8	10·56
1·0010	0·26	1·0110	2·84	1·0210	5·43	1·0310	8·02	1·0410	10·61
2	0·31	2	2·89	2	5·48	2	8·07	2	10·66
4	0·36	4	2·94	4	5·53	4	8·12	4	10·71
6	0·41	6	3·00	6	5·58	6	8·17	6	10·76
8	0·46	8	3·05	8	5·64	8	8·22	8	10·82
1·0020	0·52	1·0120	3·10	1·0220	5·69	1·0320	8·27	1·0420	10·87
2	0·57	2	3·15	2	5·74	2	8·33	2	10·92
4	0·62	4	3·20	4	5·79	4	8·38	4	10·97
6	0·67	6	3·26	6	5·84	6	8·43	6	11·03
8	0·72	8	3·31	8	5·89	8	8·48	8	11·08
1·0030	0·77	1·0130	3·36	1·0230	5·94	1·0330	8·53	1·0430	11·13
2	0·82	2	3·41	2	6·00	2	8·59	2	11·18
4	0·87	4	3·46	4	6·05	4	8·64	4	11·23
6	0·93	6	3·51	6	6·10	6	8·69	6	11·28
8	0·98	8	3·56	8	6·15	8	8·74	8	11·34
1·0040	1·03	1·0140	3·62	1·0240	6·20	1·0340	8·79	1·0440	11·39
2	1·08	2	3·67	2	6·25	2	8·85	2	11·44
4	1·13	4	3·72	4	6·31	4	8·90	4	11·49
6	1·18	6	3·77	6	6·36	6	8·95	6	11·55
8	1·24	8	3·82	8	6·41	8	9·00	8	11·60
1·0050	1·29	1·0150	3·87	1·0250	6·46	1·0350	9·05	1·0450	11·65
2	1·34	2	3·93	2	6·51	2	9·10	2	11·70
4	1·39	4	3·98	4	6·56	4	9·16	4	11·75
6	1·45	6	4·03	6	6·62	6	9·21	6	11·81
8	1·50	8	4·08	8	6·67	8	9·26	8	11·86
1·0060	1·55	1·0160	4·13	1·0260	6·72	1·0360	9·31	1·0460	11·91
2	1·60	2	4·19	2	6·77	2	9·36	2	11·96
4	1·65	4	4·24	4	6·82	4	9·42	4	12·01
6	1·70	6	4·29	6	6·88	6	9·47	6	12·06
8	1·76	8	4·34	8	6·93	8	9·52	8	12·12
1·0070	1·81	1·0170	4·39	1·0270	6·98	1·0370	9·57	1·0470	12·17
2	1·86	2	4·44	2	7·03	2	9·62	2	12·22
4	1·91	4	4·50	4	7·08	4	9·68	4	12·27
6	1·96	6	4·55	6	7·13	6	9·73	6	12·32
8	2·01	8	4·60	8	7·19	8	9·78	8	12·38
1·0080	2·07	1·0180	4·65	1·0280	7·24	1·0380	9·83	1·0480	12·43
2	2·12	2	4·70	2	7·29	2	9·88	2	12·48
4	2·17	4	4·75	4	7·34	4	9·93	4	12·53
6	2·22	6	4·81	6	7·39	6	9·99	6	12·58
8	2·27	8	4·86	8	7·45	8	10·04	8	12·64
1·0090	2·32	1·0190	4·91	1·0290	7·50	1·0390	10·09	1·0490	12·69
2	2·38	2	4·96	2	7·55	2	10·14	2	12·74
4	2·43	4	5·01	4	7·60	4	10·19	4	12·79
6	2·48	6	5·06	6	7·65	6	10·25	6	12·84
8	2·53	8	5·11	8	7·70	8	10·30	8	12·90

TABLE XXXV—*continued*.
Table for the Determination of E.

<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.	<i>x.</i>	E.
1·0500	12·95	1·0610	15·81	1·0720	18·69	1·0830	21·57	1·0940	24·46
2	13·00	2	15·87	2	18·74	2	21·62	2	24·51
4	13·05	4	15·92	4	18·79	4	21·67	4	24·57
6	13·10	6	15·97	6	18·84	6	21·73	6	24·62
8	13·15	8	16·02	8	18·90	8	21·78	8	24·67
1·0510	13·21	1·0620	16·07	1·0730	18·95	1·0840	21·83	1·0950	24·72
2	13·26	2	16·13	2	19·00	2	21·88	2	24·78
4	13·31	4	16·18	4	19·05	4	21·94	4	24·82
6	13·36	6	16·23	6	19·10	6	21·99	6	24·88
8	13·42	8	16·28	8	19·16	8	22·04	8	24·93
1·0520	13·47	1·0630	16·33	1·0740	19·21	1·0850	22·09	1·0960	24·99
2	13·52	2	16·39	2	19·26	2	22·15	2	25·04
4	13·57	4	16·44	4	19·31	4	22·20	4	25·09
6	13·62	6	16·49	6	19·37	6	22·25	6	25·14
8	13·68	8	16·54	8	19·42	8	22·30	8	25·20
1·0530	13·73	1·0640	16·60	1·0750	19·47	1·0860	22·36	1·0970	25·25
2	13·78	2	16·65	2	19·52	2	22·41	2	25·30
4	13·83	4	16·70	4	19·58	4	22·46	4	25·36
6	13·89	6	16·75	6	19·63	6	22·51	6	25·41
8	13·94	8	16·80	8	19·68	8	22·57	8	25·46
1·0540	13·99	1·0650	16·86	1·0760	19·73	1·0870	22·62	1·0980	25·51
2	14·04	2	16·91	2	19·79	2	22·67	2	25·56
4	14·09	4	16·96	4	19·84	4	22·72	4	25·62
6	14·14	6	17·01	6	19·89	6	22·78	6	25·67
8	14·20	8	17·07	8	19·94	8	22·83	8	25·72
1·0550	14·25	1·0660	17·12	1·0770	20·00	1·0880	22·88	1·0990	25·78
2	14·30	2	17·17	2	20·05	2	22·93	2	25·83
4	14·35	4	17·22	4	20·10	4	22·99	4	25·88
6	14·41	6	17·27	6	20·15	6	23·04	6	25·93
8	14·46	8	17·33	8	20·20	8	23·09	8	25·99
1·0560	14·51	1·0670	17·38	1·0780	20·26	1·0890	23·14	1·1000	26·04
2	14·56	2	17·43	2	20·31	2	23·20	2	26·09
4	14·61	4	17·48	4	20·36	4	23·25	4	26·14
6	14·67	6	17·54	6	20·41	6	23·30	6	26·20
8	14·72	8	17·59	8	20·47	8	23·35	8	26·25
1·0570	14·77	1·0680	17·64	1·0790	20·52	1·0900	23·41	1·1010	26·30
2	14·82	2	17·69	2	20·57	2	23·46	2	26·35
4	14·87	4	17·75	4	20·62	4	23·51	4	26·41
6	14·93	6	17·80	6	20·68	6	23·57	6	26·46
8	14·98	8	17·85	8	20·73	8	23·62	8	26·51
1·0580	15·03	1·0690	17·90	1·0800	20·78	1·0910	23·67	1·1020	26·56
2	15·08	2	17·95	2	20·83	2	23·72	2	26·62
4	15·14	4	18·01	4	20·89	4	23·77	4	26·67
6	15·19	6	18·06	6	20·94	6	23·83	6	26·72
8	15·24	8	18·11	8	20·99	8	23·88	8	26·78
1·0590	15·29	1·0700	18·16	1·0810	21·04	1·0920	23·93	1·1030	26·83
2	15·35	2	18·22	2	21·10	2	23·99	2	26·88
4	15·40	4	18·27	4	21·15	4	24·04	4	26·93
6	15·45	6	18·32	6	21·20	6	24·09	6	26·99
8	15·50	8	18·37	8	21·25	8	24·14	8	27·04
1·0600	15·55	1·0710	18·43	1·0820	21·31	1·0930	24·20	1·1040	27·09
2	15·61	2	18·48	2	21·36	2	24·25	2	27·15
4	15·66	4	18·53	4	21·41	4	24·30	4	27·20
6	15·71	6	18·58	6	21·46	6	24·35	6	27·25
8	15·76	8	18·63	8	21·52	8	24·41	8	27·30

TABLE XXXVI. (*Text*, p. 825.)Reducing Values for Dextrose, Lævulose, Invert Sugar,
and Maltose. (Ling and Jones.)

Volume of solution required by 10 c.c. Fehling's solution.	Dextrose.		Lævulose.		Invert sugar.		Maltose.	
	D. Dextrose in 100 c.c. of solution.	D'. Fehling's solution equivalent to 1 g. dextrose.	L. Lævulose in 100 c.c. of solution.	L'. Fehling's solution equivalent to 1 g. lævulose.	I. Invert in 100 c.c. of solution.	I'. Fehling's solution equivalent to 1 g. invert.	M. Maltose in 100 c.c. of solution.	M'. Fehling's solution equivalent to 1 g. maltos.
c.c.	g.	c.c.	g.	c.c.	g.	c.c.	g.	c.c.
20	0.2427	206.0
21	0.2332	205.1	0.2412	197.5	0.3888	122.5
22	0.2226	204.2	0.2411	188.5	0.2311	196.8	0.3711	
23	0.2138	203.4	0.2312	188.0	0.2218	196.0	0.3550	
24	0.2056	202.6	0.2222	187.5	0.2132	195.5	0.3402	
25	0.1981	201.9	0.2138	187.1	0.2052	194.9	0.3266	
26	0.1911	201.3	0.2060	186.7	0.1980	194.3	0.3140	
27	0.1846	200.7	0.1988	186.3	0.1910	193.9	0.3023	
28	0.1784	200.1	0.1921	186.0	0.1846	193.4	0.2915	
29	0.1728	199.6	0.1857	185.6	0.1787	193.0	0.2815	
30	0.1675	199.1	0.1798	185.4	0.1731	192.5	0.2721	
31	0.1625	198.6	0.1743	185.1	0.1678	192.2	0.2633	
32	0.1577	198.2	0.1691	184.8	0.1629	191.8	0.2551	
33	0.1532	197.8	0.1642	184.6	0.1583	191.5	0.2474	
34	0.1490	197.4	0.1596	184.3	0.1539	191.2	0.2401	
35	0.1450	197.0	0.1552	184.1	0.1497	190.9	0.2332	
36	0.1412	196.7	0.1511	183.9	0.1458	190.6	0.2268	
37	0.1377	196.4	0.1472	183.6	0.1421	190.3	0.2206	
38	0.1343	196.0	0.1435	183.4	0.1385	190.1	0.2148	
39	0.1310	195.8	0.1399	183.3	0.1349	189.8	0.2093	
40	0.1279	195.5	0.1366	183.1	0.1319	189.6	0.2041	122.5
41	0.1334	182.9	0.1288	189.4
42	0.1298	182.8	0.1259	189.2
43	0.1274	182.6

A constant

TABLE XXXVII. (*Text*, p. 834.)

Spirit Indication Table showing Degrees of Gravity Lost in Malt Wort during Fermentation.

Degrees of spirit indication.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	...	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·4	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	71·1	71·7	72·3	72·9	73·5	74·1	74·7	75·3	75·9

TABLE XXXVIII. (*Text*, p. 834.)

Acid Correction Table showing Additions to be made to Spirit Indication for Small Increments of Acidity in excess of 0·1 per cent.

Excess per cent. of acetic acid in beer.	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
·0	...	0·02	0·04	0·06	0·07	0·08	0·09	0·11	0·12	0·13
·1	0·14	0·15	0·17	0·18	0·19	0·21	0·22	0·23	0·24	0·26
·2	0·27	0·28	0·29	0·31	0·32	0·33	0·34	0·35	0·37	0·38
·3	0·39	0·40	0·42	0·43	0·44	0·46	0·47	0·48	0·49	0·51
·4	0·52	0·53	0·55	0·56	0·57	0·59	0·60	0·61	0·62	0·64
·5	0·65	0·66	0·67	0·69	0·70	0·71	0·72	0·73	0·75	0·76
·6	0·77	0·78	0·80	0·81	0·82	0·84	0·85	0·86	0·87	0·89
·7	0·90	0·91	0·93	0·94	0·95	0·97	0·98	0·99	1·00	1·02
·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

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